Enamels and Enamelling

AN INTRODUCTION TO THE PREPARATION AND APPLICATION
OF ALL KINDS OF ENAMELS FOR TECHNICAL AND
ARTISTIC PURPOSES

FOR ENAMEL MAKERS, WORKERS IN GOLD AND SILVER,
AND MANUFACTURERS OF OBJECTS OF ART

BY

PAUL RANDAU

TECHNICAL CHEMIST

TRANSLATED FROM THE GERMAN BY

CHARLES SALTER

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PREFACE

As in all other branches of industry founded on a chemical basis, a number of novelties have arisen in connection with enamel-making during the past few years. It would at the first glance appear advisable to have included these novelties, on an extensive scale, in revising the present work for this third (German) edition; but, as novelty is not always synonymous with improvement, the author has preferred to restrict himself to such of the said novelties as have proved reliable when tested, his principal desire being to maintain conciseness and brevity in dealing with his materials—qualities indispensable to a book intended to act as a useful adviser to the practical man.

There are two questions of great importance to the enamel manufacturer. One concerns the means whereby the consumption of fuel may be reduced to a minimum; the other relates to the decoration of white enamel articles. Both these points have been considered on an extended scale in the present edition, and the practical man will be able to form a sound opinion on the nature of the case from the information given.

Having received gratifying testimony from many experts as to the reliable advice on the preparation and use of enamels afforded in the earlier editions, the author has not greatly altered the arrangement and treatment of the different sections in revising the present edition, the additions he considered necessary being mainly confined to methods of firing and to the decoration of the finished enamelled ware; and he trusts that the new edition will meet the same favourable reception as already accorded to the work. Any information relating to novelties in the domain of the enamel industry will be thankfully received and utilised for the common weal in preparing a future edition.

PAUL RANDAU.

ENAMELS AND ENAMELLING.

I.

INTRODUCTION

THE art of covering metallic and other articles with a coating, mostly composed of some coloured glaze, is one of considerable antiquity, and appears to have long been practised by the cultivated peoples of Eastern Asia, *viz.*, the Chinese and Japanese. How long this same art has been known to Europeans cannot be definitely stated, but that the practice has been in vogue for several centuries is evidenced by the presence, in different European museums, of variously coloured specimens of enamelled work, most probably executed by Byzantine artists.

Ancient records and the discoveries made in Egyptian, Grecian and Italian ruins, afford plenty of evidence that the ancient Egyptians were acquainted with coloured glasses and enamels, and knew how to manufacture them in various shades, which knowledge appears also to have been shared by the Greeks, who in many of the arts and sciences were pupils of the Egyptians. Thus Democritus of Abdera, who flourished in the fifth century before our era, is said to have discovered how to make imitation emeralds, and therefore must have been acquainted with the materials used for imparting a green coloration to glass.

The Roman, Pliny, to whom we are indebted for his compilation on the condition of the natural science and technical knowledge of the age, makes repeated mention of coloured glass, and states that perfectly colourless glass, approaching rock crystal in clearness, was held in the highest estimation.

The materials employed by the ancients for colouring glass and enamel were precisely the same as those used at the present time, the chemical analysis of antique coloured glasses and fluxes showing that red was produced by cuprous oxide, green by cupric oxide, and blue by means of cobalt. To what extent the development of the art of glass-making had attained among the ancients is evident from the circumstance that they were thoroughly aware of the decolorising effect of manganese oxide on glass coloured green by iron, and made use of this body for purifying the glass.

The art of manufacturing decorative articles, vessels, weapons and other objects, had already attained a high degree of perfection in the Orient at the time when the Crusades brought Europeans into closer contact with the inhabitants of Western Asia; and it was most probably through the Crusaders returning from the Holy Land that these arts first became domiciled in France and Italy.

A stimulative effect on the knowledge of the art of making glass and enamel was exercised by the development of alchemy, the followers of which science discovered, as a kind of by-product, methods of preparing differently coloured glass fluxes in the slag they only too frequently obtained in place of the gold anticipated.

The first precise indications on the means of imparting colour to glass fluxes were given by the alchemist Porta, in his work *Magia Naturalis* (1567), which contained sundry recipes on this subject. Moreover, the art of making enamels had already at that time arrived at a high degree of eminence in Italy, evidence of which is afforded by still existing glass mosaics of the period, the work of Venetian artists.

Information on the production of enamelled articles in particular was also given by Porta, as well as by a contemporary alchemist B Palissy, the latter in his work *De l'art de terre.* It is probable that the use of tin had been known already in earlier times as an important constituent of various enamels, the ancient Greeks and Romans having been well acquainted with this metal, which was obtained by the Phœnicians from Britain.

Whilst up to the beginning of the present century the use of coloured glass fluxes and enamels was confined to the decoration of articles of value and jewellery, in more recent times an industrial application has been found for enamel, as a coating for iron to enable the metal to withstand the influence of chemical reagents In this connection specially good service has been rendered by Pleischl, of Vienna. It should not be forgotten, however, that a special, though somewhat restricted, industrial application of enamel has existed for a considerable time, namely the enamelling of clock dials, which operation consists in coating a metallic (generally copper) substratum with a white (fused) enamel.

In addition to covering domestic utensils (saucepans, etc.), and vessels for the manufacture of chemical preparations, enamel is now frequently used for coating the tubes of locomotive and marine boilers, water-pipes, and iron stoves (which thereby acquire the external appearance of fine porcelain), as well as for various other purposes. The circumstance that enamel will not hold except on a surface of gold, copper, or iron, which is the reason why its use was formerly limited to articles made of these metals, is now no longer an impediment to its application to other metals, since by means of electro-plating, the latter can be covered by a thin layer of copper on which the enamel can be laid.

The enamelling of iron on a large scale dates back no further than about fifty years, and those at first engaged in the industry contrived to keep their methods secret for a considerable time. Now, however, though many makers still lay claim to the possession of special enamelling recipes known only to themselves, such claims may be regarded as intended merely for purposes of self-advertisement, since nowadays any one who has studied chemistry and has an extensive knowledge of glass-making, is, after careful examination of any enamel, and after a series of experiments based on the result, in a position to imitate an original to perfection, and to prepare enamels of thoroughly definite colour, fusibility, etc.

Chemical knowledge, however, is not at present so widespread in industrial circles that one can proceed to describe the manufacture of enamels with a presumption that one's hearers or readers are fully acquainted with everything relating to the metallic oxides and glass. Consequently, in order to adapt the present work to the needs of those who are deficient in a thorough knowledge of chemistry, the author considers it important to first give some general information as to the nature of glass and the properties of such metallic oxides as find employment in the preparations of enamel. The necessity for dealing more particularly with glass arises from the nature of the enamels themselves, since these bodies consist of glass which, by suitable admixtures, is rendered either transparent or perfectly opaque; this glass forms the basis of every enamel, and is itself really enamel—in fact the most generally used white enamel—which can be converted by the employment of suitable pigments into the various coloured enamels.

The capacity of enamel to withstand fluctuations of temperature and the action of chemicals, is chiefly dependent on the constitution of the glass basis. One is therefore perfectly justified in saying that no one can make really good enamels unless thoroughly acquainted with the nature of glass, and in a position to prepare glass masses of the constitution requisite for the purpose of making enamel.

The raw materials for this purpose may be divided into three groups: (1) Those required for the production of glass; (2) those used to convert the glass into an enamel of a given colour; (3) those serving to increase the fusibility of the product.

II.

THE COMPOSITION AND PROPERTIES OF GLASS.

In point of chemical composition every glass must be regarded as a mixture of two or more salts, there being, really, only one exception to this rule, *viz.*, the so-called "water glass" which consists of a single salt. Formerly silica was the only acid body employed to combine with the basic substances present in glass; but at the present time boric acid is also used in some kinds of glass, a matter of some importance in connection with the object now in view, since this last-named acid has considerable influence on certain of the properties with which glass is endowed. One result of the use of boric acid is that, whereas formerly glass could be considered as a mixture of silicates alone, this point of view now requires modification, according to circumstances, and glasses containing boric acid must be characterised as borosilicates.

At one time the bases employed in glass-making were few in number, and consisted solely of potash, soda and lime, so that the product could be entitled either a silicate of potash and lime, or a silicate of soda and lime. Nowadays, however, white glass contains, in addition, zinc oxide and lead oxide, which are used to impart certain qualities to the product.

The bases just named share with magnesia the property of forming with silica colourless compounds which can be melted or fused by exposure to a suitable degree of heat. Other bodies, such as alumina, are, it is true, also capable of forming colourless compounds with silica, but are not suitable for glass-making—the melting-points of their silicates being higher than the temperature attainable in glass furnaces.

In addition to the colourless glasses there is another series exhibiting certain shades of colour. The silicates of iron, cobalt, copper, manganese, etc., for example, possess highly characteristic colours, a property utilised in analytical chemistry to detect the presence of the oxides of these metals by the coloration they impart to certain fluxes before the blowpipe.

The colour of these last-named silicates is so intense as to generally appear quite black, the true colour only becoming apparent when the pure silicates are attenuated or diluted by admixture with others that are colourless. Thus, for example, to produce a glass tinted blue by cobaltous oxide, a colourless glass mass must be mixed either with a cobalt compound or with a glass already deeply coloured with cobalt.

Certain oxides and other compounds are insoluble in glass, and consequently by their aid one can convert colourless glass into a perfectly white or semi-translucent porcelain-like mass. The bodies most frequently employed for this purpose are calcium phosphate (in the form of bone ash) and tin oxide. It is exclusively to this class of glass that the enamels belong, and on that account they will be more completely dealt with later.

Glass may be divided into five classes, in accordance with its chemical composition, *viz.*

1. Glass with one or two bases of the same group: water glass (potassium and sodium silicate).

2. Glass containing several bases of different groups:—

   a. Lime glass.—Soda-lime glass or potash-lime glass.

   b. Lead glass.—Lead-sodium silicate.

3. Coloured glasses: soda-lime glass with an addition of oxides forming coloured compounds with silica

4. Opaque glasses: soda-lime glass containing bone ash or tin oxide.

5. Opaque coloured glasses: soda-lime glass (frequently, also mixed with lead glass) containing bone ash or tin oxide, and coloured with metallic oxides.

Classes 4 and 5 are the kinds with which we have most concern, those of class 4 forming the white enamels, whilst all the coloured enamels are comprised in class 5.

The most prominent of the general properties of glass is its indifference towards chemicals, and it is precisely this quality which is of such importance in the industrial employment of enamels.

With the exception of hydrofluoric acid and the caustic alkalies, no chemical reagent has any apparent influence on properly constituted glass unless the exposure be prolonged for years, consequently, it may rightly be said that glass is insusceptible to chemical influences, apart from the bodies just referred to. This property of indifference is, however, only met with in perfection in the potash-lime glasses, those containing lead having an inferior capacity of resistance; and enamels are again inferior to the latter, because usually less attention is bestowed on their possession of this quality than on their ready fusibility.

In connection with enamels, however, one should bear in mind the purposes for which they are intended. Thus, when it is merely a question of embellishing an artistic or decorative article, then durability becomes a relatively unimportant matter, since such articles are never exposed to the full influence of the weather, consequently the composition of the enamel need not be specially designed with a view to ensuring durability or resisting power.

On the other hand, the conditions are different for enamels destined to protect the surface of metals from the action of chemicals, beauty of colour being in such event a minor consideration in comparison with power to withstand external influences.

The property of resistance in both glass and enamel entirely depends on their chemical composition, properly constituted glasses being able to withstand the action of the atmosphere for centuries without appreciable injury; whilst if defective, only a very few years will elapse before peculiar symptoms of decomposition will become manifest—the glass becomes dull, even opaque, and thin scales peel off, this occurrence being preceded by iridescence. The last phenomenon is due not to the formation of coloured compounds but to a special property possessed by extremely thin strata of colourless bodies, and one that is particularly well exemplified in the case of soap bubbles. After the separation of these scales the glass appears dull, and exhibits an uneven surface.

This decomposition is the result of the action of atmospheric carbonic acid (carbon-dioxide) which dissolves a portion of the alkali base and liberates silica. The subjoined analyses of the external layers and inner portion of an antique Roman glass vessel plainly indicate the similarity between this decomposition and the weathering of silicate rocks.:—

	External layer	Internal mass
Silica	18·8	59·2
Alumina	3·4	5·6
Lime	11·3	7·0
Magnesia	6·8	1·0
Ferrous oxide	11·3	2·5
Manganous oxide	trace	trace
Soda	—	21·7
Potash	—	3·0
Moisture	19·3	—

Many kinds of glass become dull ("blind") suddenly, for the most part after exposure to moderate warmth. This is frequently observable in the case of potash glass, and is due to the formation of an aqueous silicate. The prolonged action of hot water seems to corrode every kind of glass to a greater or smaller extent; and, if conjoined with high pressure, leads to total decomposition of the glass, which yields up alkali to the water and becomes converted into an earthy-looking mass of particularly tender crystals.

Alkaline liquids, and particularly the concentrated caustic alkalies, attack glass the most, the first effect produced being the formation of innumerable tiny fissures which gradually extend throughout the entire substance of the glass. As the enamels in general belong to the least resistant type of glass, special care must be taken not to employ enamelled vessels for heating solutions of caustic alkalies.

The effect produced on glass varies according to the reagent employed; and in this connection the following results obtained by a series of experiments will not be devoid of interest, especially as they are also generally applicable to enamels.

In the case of many kinds of glass the energy of the reaction is most pronounced at the outset, and increases very rapidly as the temperature is raised Alkalies, even in dilute solutions, corrode glass very extensively, whilst dilute acids are less corrosive than water—except dilute sulphuric acid, which is more powerful than the latter. Salts containing acids which form insoluble compounds with lime, attack glass more vigorously than water does, the effect varying directly with the concentration of the solution—to this class belong the salts of the alkali metals with sulphuric acid, phosphoric acid, carbonic acid and oxalic acid. Chlorides and nitrates, on the other hand, have but little influence, the effect decreasing as the solutions are more highly concentrated.

The resisting power of lead glass is unusually small, the glass being attacked by substances entirely without action on other kinds of glass. Even sulphuretted hydrogen or ammonium sulphide is strong enough to spoil the transparency of lead glass, which, under their influence, turns grey from the formation of lead sulphide. Unfortunately, many enamel manufacturers regard the addition of a considerable proportion of lead glass as inevitable, being of the erroneous opinion that this is the sole efficacious method of obtaining a sufficiently fusible product.

Although it is indisputable, that for certain purposes of the enamelling industry an addition of lead glass to the mixture cannot be dispensed with, it should nevertheless be as small as possible, and especially for enamels intended for use on cooking utensils, lead preparations being undesirable for such ware.

Another point that cannot be too closely looked after by makers of enamels is the behaviour of the glass when heated, as it depends entirely on the composition of the glass mass whether the enamel coating of a cooking utensil will remain unaltered for a considerable time or will crack or peel off after the article has been a little while in use

Unless composed of specially refractory materials, the glass mass, on exposure to very high temperatures, will become as thin in consistency as moderately concentrated syrup The molten mass becomes thicker and thicker in proportion as the temperature is reduced, and thus the consistency can be changed at will by regulating the temperature.

When glass is cooled down very quickly, it becomes so brittle that a slight shock is often sufficient to make it crack or fly. Glass prepared in this manner is totally unfit for any technical purpose, careful and protracted cooling (annealing) at a slow rate being necessary, as the sole means of attaining the requisite degree of elasticity.

In the case of enamels proper, cooling is a still more important matter, owing to the fact that the metal surface with which the enamel is in such close connection expands when warmed and contracts again on cooling; consequently, unless the enamel is able to assimilate to this motion of the underlying metal it will inevitably lose its coherence, and in a very short time will be traversed by innumerable small cracks.

When glass is maintained for a considerable length of time at a temperature very near to fusing point, the phenomenon known as devitrification occurs, the mass becoming dull and opaque, whilst at the same time its hardness greatly increases, so that in some instances the glass will strike fire with steel.

The cause of devitrification is to be sought in the circumstance that, during the protracted transition from the fluid to the solid state a portion of the silicates in the glass crystallises, and thereby imparts a semblance of porcelain to the whole A closer examination of the glass reveals the presence of colourless crystals in the colourless matrix, the opacity of the whole being the result of a difference of refractive power between the two, the degree of which influences the appearance of the glass so that the latter may even seem quite white.

Another very peculiar phenomenon, hitherto unexplained, is the action of light on glass. It is known from a number of casual observations and more thorough experiments that glass, on exposure to light, either changes in shade if previously coloured, or, if colourless, acquires a tinge of colour. Thus, for example, glass that has been decolorised by manganese compounds turns a beautiful violet shade after prolonged exposure to light. As this is a matter of some importance for enamels as well, particularly those in delicate colours, the results of the observations made on the colour changes undergone by different kinds of glass, are now given :—

	Before	After
	Exposure to Light	
French sheet glass	Bluish white	Yellowish
German crystal glass	Faint green	Bluish tinge
English sheet glass	,, ,,	Yellowish green
,, crown glass	,, ,,	Faint purple.
Belgian window glass	Brownish yellow	Dark purple
English ,, ,,	Dark green	Brownish green.
American crystal glass	White, faint bluish tinge	White purple.
,, ,, ,,	,, ,, ,, ,,	Faint yellowish green.
Ordinary American glass	Bluish green	Unchanged.

Taken altogether, the foregoing general remarks on the properties of glass apply equally to enamels; and special attention should again be directed to the necessity of selecting the materials for technical enamels, so that the mass exhibits a minimum of susceptibility to the action of chemicals, and at the same time possesses a coefficient of expansion sufficient to preclude the risk of cracking when in use

III.

RAW MATERIALS FOR THE MANUFACTURE OF ENAMELS.

The raw materials worked up into enamel are numerous and diverse in character, the production of the various coloured enamels necessitating the employment of many substances not generally used for glass-making. They may all, however, be divided into two main classes: the general or fundamental materials, essential to every enamel; and the particular substances required to impart certain definite qualities—fusibility and colour—to special kinds of enamel. The first class may be termed fundamental, and the second supplementary, materials; a third class, of subsidiary materials, comprising certain substances used in applying the enamel, though not in the actual process of manufacture

Fundamental Materials

Since, as has already been stated, enamels should be reckoned as being in the same category with glass, it follows that their production necessitates the use of the same materials as are used in glass-making.

Ordinary glass consists, as mentioned above, of soda, lime and silica, or potash, lime and silica, or of mixtures of these silicates, lead silicate, in addition, forming an important constituent of many kinds such as the so-called flint glass and crystal glass. The small, though inevitable, proportion of extraneous impurities such as ferric oxide, may be dismissed from consideration as merely accidental, especially in fine white glass. Consequently, the materials used for making glass must contain one or other of the above-mentioned compounds.

The matrix of enamel must also contain a very finely divided infusible white substance, generally tin oxide or bone ash, to render the glass opaque and, as one or other of these is an essential constituent of all enamels, they must also be reckoned among the fundamental materials As the success of the resulting product depends on the suitability of these materials, a more precise account of their properties and method of preparation will now be given

Silica.

This substance is one of the most extensively distributed bodies met with in our planet, being not only a main constituent of the rocks (*e g* granite and gneiss) forming the highest and largest mountains in the world, but also occurring in a pure state in numerous deposits.

The minerals, rock crystal, quartz and quartz sand, as well as flint, consist of almost perfectly pure silica; as do also the minerals known under the names of amethyst (violet), citrin (yellow), smoky topaz and morion (smoke brown to black), the only admixture being the minute proportion of extraneous matter producing the particular colour in each case

From the chemical point of view, silica is composed of silicon (Si) and oxygen (O_2) SiO_2 There are two allotropic modifications of this body . the crystalline (found almost pure, as rock crystal and quartz), and the amorphous form—*e g*, flint, hyalite and opal.

Silica belongs to the class of bodies that are infusible when heated alone It is inert towards other substances, and is unattacked by the strongest acids; in fact there are only two bodies capable of acting upon it at all, *viz.*, hydrofluoric acid and the alkalies. On boiling quartz in a solution of caustic potash or caustic soda a considerable part of the silica passes into solution; and if silica be fused along with potash, soda or an alkaline earth (lime) it readily combines with them to form more or less refractory compounds (silicates), a reaction on which the manufacture of glass and enamels is based.

At the ordinary temperature silica is such a weak acid that it can be displaced from its soluble compounds even by carbonic acid, solutions of the so-called water glass (sodium silicate) quickly setting, when exposed to the air, to a gelatinous mass in consequence of the atmospheric carbon-dioxide causing the precipitation of the silica in a hydrated condition (soluble silica) as a voluminous mass.

On the other hand, at high temperatures, silica, by reason of its non-volatility, forms the most powerful acid known. At a strong red heat it will readily displace sulphuric, and even phosphoric, acid from their respective compounds—a property which is often utilised in glass-making by replacing the pure alkalies by their sulphatic salts.

The principal varieties of silica coming under consideration for our purposes are quartz, quartz sand and flint; rock crystal being the very best of all when available, though as a rule it is too costly to be dreamed of as a material for the manufacture of glass or ordinary enamels. When, however, it is a question of producing a small quantity of fine enamel, especially such as are required to be of very delicate shades of colour, then rock crystal should always be used, as it greatly facilitates the work.

The quartz sand encountered in extensive deposits on the shores of rivers, etc., is usually derived from quartz-bearing rocks that have been broken up and transported by the force of water. When the sand is very white it originated in quartz rock, and forms an excellent raw material for enamels and fine white glass; and, moreover, requires but little preparatory treatment to render it fit for use

Quartz sand resulting from the decomposition of granite or gneiss, mostly contains small quantities of the minerals associated with quartz in these rocks. These minerals, however, are felspar and mica, the former in the state of (generally white) crystals, whilst the latter is generally in the condition of very fine crystalline flakes, green or black in colour. The presence of these impurities in quartz sand greatly reduces the value of the latter for our purpose, since, on the one hand, they considerably diminish the fusibility of the glass, and, on the other hand, mica imparts a strong coloration to the product As it is a difficult, and on a large scale impracticable, operation to purify the quartz sand from these admixtures, such sands must be discarded when the production of fine glass is in question, though they may be advantageously employed for making commoner qualities.

In many places fine-grained sandstones are met with, consisting almost entirely of pure quartz sand, the individual grains of which are cemented together by a relatively small amount of lime When treated in a suitable manner to get rid of this lime sandstones of this class form a very useful source of silica for glass- or enamel-making

An excellent material for enamels and fine glass is afforded by the so-called infusorial or diatomaceous earth (Kieselguhr) which occurs as a fine, nearly pure white mass, so soft as to be easily reduced to an almost impalpable powder by rubbing between the fingers Microscopic examination shows this wrongly named "infusorial earth" to consist of the siliceous integument of diatoms, polythalamia and other lower organisms, the organic constituents of which have entirely disappeared, leaving behind only the outer shells of nearly pure silica.

For the purposes of the glass-maker, however, diatomaceous earth is a somewhat troublesome material to deal with in working on a large scale, being so bulky as to give rise to considerable difficulty in charging the pots. This difficulty disappears when the production of fine enamels is in question, and for this purpose the use of diatomaceous earth is highly advisable.

Many kinds of quartz and quartz sand would be well adapted for the manufacture of glass were it not for their content of compounds of iron which give rise to an undesirable coloration of the product. In many cases this difficulty can be obviated in the manner described below, and a simple test for the direct suitability of a given sample of quartz material consists in exposing a portion of the same to a strong red heat and comparing its colour, after cooling, with that of the original sample If the colour is unaltered, or has merely acquired a yellowish tinge, then the quartz may be regarded either as perfectly free from iron or as containing merely a negligible quantity of that metal. On the other hand, if it has changed to a decided red, the presence of a large amount of iron oxide is indicated, and the quartz must either be used solely for common glass, or else be subjected to purification

Purifying Quartz

This operation consists in suffusing the finely pulverised quartz with a mixture of equal parts of crude hydrochloric acid and water, the liquid being poured off again after a short time, and the quartz afterwards washed repeatedly with water. The iron oxide present will be dissolved by the hydrochloric acid, provided the quartz has not previously been very strongly calcined, if, however, the iron is in the form of silicates, these compounds will not be decomposed by the acid, and will impart a brown coloration to the glass in the subsequent stage of melting the mass.

This hydrochloric acid treatment, however, being rather expensive, and, as we have seen, not always attended with the desired result, cannot be specially recommended; and it is preferable—for fine white or good coloured enamels—to pick out the best colourless quartz and use this by itself.

In preparing enamels for technical purposes the chief point to be regarded is the power of withstanding the action of chemical and rapid changes of temperature, colour being a subordinate consideration; consequently, in such cases, the selection of the quartz need not be looked after so strictly, since a slight yellow tinge will do no harm, and will, moreover, be for the most part masked by the white components in the matrix. For enamels for coating the inside of cooking utensils, where a pure white colour is more particularly required, no trouble should be spared in sorting out a very pure grade of quartz or even in procuring the same from a distance, as the better colour of the enamel and higher value of the ware will more than compensate for the greater initial outlay.

Sedimentation

A very useful method of freeing quartz sand from extraneous admixtures is that of washing by sedimentation, which is particularly advisable when, as not infrequently happens, the chief impurity is clay. It may be stated here that the silicates of alumina form glasses of exceedingly high fusing point, and consequently these bodies require to be eliminated from quartz sand intended for the production of enamels.

The washing is effected in a very simple arrangement of wooden tubs provided with tap holes at different heights. One of these tubs is filled about three parts full with clean water, which is stirred round and round while the sand is run in. As soon as this is done the stirring is discontinued, and, after waiting a few minutes until it seems probable that the sandy particles have settled down, the uppermost tap hole is opened and the water run off.

When the sand contains clay, the particles of which float in suspension much longer than those of the quartz, the water runs away quite muddy, and the tap holes are opened in succession until the tub is empty; whereupon the taps are shut again and a fresh supply of water is added, the sand being stirred up once more and the settling and washing repeated until finally the added water runs away perfectly clean—a proof that all the clay has been washed out.

To preserve the washed sand from contamination it is shovelled out of the tubs with wooden shovels and packed in strong canvas cloths until air-dry, whereupon it is stored in tightly closed wooden bins until required for use. Iron shovels must not be used, the hard quartz wearing them out by attrition, whereby the sand becomes contaminated with iron in sufficient (though small) amount to produce an appreciable coloration of the glass made from such sand.

Quenching.

To fit rock crystal, quartz rock, or flint for use in glass- or enamel-making, these materials must be subjected to a process of comminution to bring them into the condition of coarse meal, because larger granules of quartz are only dissolved with difficulty by the glass mass and will be readily discernible in the finished product. Now, to grind down large quantities of a mineral like quartz, which is of the seventh degree of hardness, would require a truly gigantic expenditure of force; and therefore to enable the reduction to be effected with a smaller consumption of power the material is first subjected to heating, followed by a rapid process of cooling.

When rock crystal, quartz rock or flint is strongly calcined and then at once thrown into water, the cooled lumps exhibit innumerable fine cracks both on the surface and throughout the mass. The sudden contraction ensuing on the contact of the glowing material with water is so extensive in the superficial layers as to overcome the cohesion of the particles and to produce an infinite number of cracks, through which the water gains access to the still glowing interior, whereby it is converted into steam, which forces the particles of quartz asunder by its expansion

This method of sudden cooling is known in practice as "quenching," and if a lump of quartz that has been treated in this way is struck with a hammer, it breaks up into a number of small fragments easily reducible to a fine powder

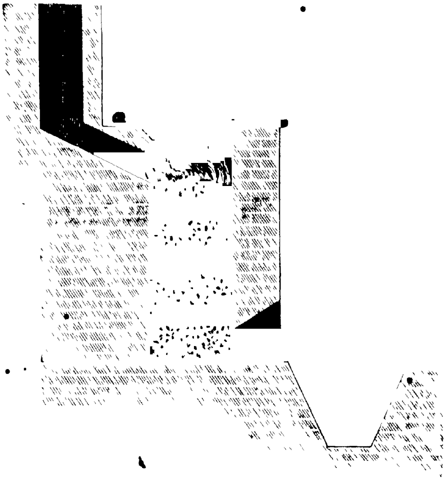

Fig. 1

The furnaces used for calcining quartz are very simple, a useful type being shown in Fig. 1. The cylindrical shaft of fireproof material, about 16-20 inches in diameter and 60 to 80 inches high, is closed at the top by a hinged cover of cast iron lined with fireclay. Below, at the front of the furnace, is an aperture of the same width as the internal diameter of the shaft and about 8 inches high, which can be closed by a door provided with a damper, and in front of this opening is a brick-lined pit filled with water. Immediately underneath the top cover, the shaft communicates with a chimney capable of producing a good draught.

The shaft is first charged, about one-third full with glowing coal, which is then covered with a layer of the quartz to be calcined. Another stratum of fuel is spread on the top of this, and the shaft is filled up to the top with alternating layers of quartz and fuel. The amount of the latter required properly to calcine a given weight of quartz has to be determined by experiment.

As soon as the lower charge of fuel is consumed and the glowing quartz has sunk to the bottom of the shaft, it is raked quickly out of the furnace and falls into the quenching pit; and in proportion as the lower charges of quartz are removed, the shaft is replenished by adding more quartz and fuel at the top. By this means the furnace is kept continuously in action, so that very large quantities of quartz can be quenched in a short time and with a minimum consumption of fuel. The quenched quartz is next broken down into coarse powder in a stamping mill, and is then screened, the coarser particles being returned to the stamps, while the remainder, passing through the fine-mesh screen, is ground to fine meal.

Although the mechanical reduction of such a hard mineral as quartz is rather expensive, the operation is one requiring extreme care since it facilitates the production of perfect homogeneity in the subsequent fusion of the enamel mass

THE ALKALIES.

The second class of indispensable constituents for glass and enamel is that of the alkalies. As already mentioned silica, when fused with a single alkali, forms a mass which bears the name of glass (water glass) but is distinguishable from all other kinds of glass by its solubility in water; and it is only when an alkaline earth (lime) or an oxide of some heavy metal (lead oxide) is added that the product usually known as glass is obtained.

For our purpose the alkalies can be used in the form of various compounds, because, as already stated, silica decomposes all these combinations at a red heat, and seizes upon the alkali for itself. For glass-making the compounds of both potash and soda can be utilised, but, generally speaking, the last named alone is employed in the preparation of enamels—the potash glasses, though more resistant than those made from soda, being too refractory for our purpose

The potassium and sodium compounds generally employed are as follows —

A. *Potassium Compounds.*

Potash (impure potassium carbonate K_2CO_3).

Wood ashes (a mixture of salts of calcium, magnesium, potassium and sodium, together with small quantities of iron oxide) The soluble part of wood ashes consists mainly of potassium carbonate.

Sulphate of potash or potassium sulphate, K_2SO_4 (by-product from certain chemical processes).

B. *Sodium Compounds*

Common salt (sodium chloride, NaCl)

Soda (sodium carbonate, Na_2CO_3)

Kelp (impure sodium carbonate).

Glauber salt (sodium sulphate, Na_2SO_4, manufactured, and also obtained as a by-product in nitric acid works).

Pan stone (a mixture of variable quantities of sodium sulphate and calcium sulphate $CaSO_4$ chipped out of salt pans in the process of cleaning).

A. POTASSIUM COMPOUNDS.

Potash.

In countries where wood is abundant, potash is obtained by lixiviating wood ashes, evaporating the extract to dryness, and calcining the residue. This "calcined potash" is of a greyish blue or reddish colour, due to the presence of compounds of manganese or iron from the wood. The yellow or red tinge is particularly objectionable because the ferric oxide contained in such potash is a very strong pigment; and consequently, since this body influences the colour of glass, such high-coloured grades of potash should not be used in the preparation of enamels. Moreover, potash entirely free from iron and therefore admirably adapted for our purpose, can now be obtained in commerce. Potash belongs to the class of strongly hygroscopic substances, and must therefore be stored in tightly-closed barrels lined with paper.

Wood Ashes.

Wood ashes may be regarded as potash containing, in addition to the usual saline matter, a certain, though small quantity of carbon, to which the greyish colour of the mass is due. As this carbon and the iron compounds present unfavourably affect the colour of glass, ordinary wood ashes should only be used for making common glass

Sulphate of Potash

Formerly this salt was more frequently obtained as a by-product of nitric acid manufacture than at present, because it was then the practice to make this acid from saltpetre (potassium nitrate) exclusively, whereas now, the cheaper nitrate of soda is almost always used in making nitric acid.

Since the effect of potash salts is to reduce the fusibility of glass, they are seldom employed in the preparation of enamels. Nevertheless, for special enamels required to withstand the action of chemicals, potash is used though in the form of felspar (which contains potassium silicate) and not as the above-named salt.

B SODIUM COMPOUNDS.

Common Salt (Sodium Chloride).

This substance is obtained from salt mines, either in the crude form of rock salt or in the manufactured (purified) condition, the former containing gypsum and clay, and being coloured grey or yellow by compounds of iron. Salt is not much used in enamel-making, since other sodium compounds better suited to the purpose can be obtained at low rates

Soda (Sodium Carbonate)

This chemical product which is manufactured in enormous quantities in special works, is met with in commerce in two forms soda crystals and calcined (or anhydrous) soda. The former kind is in large water-white colourless crystals, which, however, on prolonged exposure in the air, become covered with a white incrustation, and finally fall entirely into the state of powder, the change being attended with a great loss in weight. This is due to the evaporation of the water of crystallisation, though a certain proportion of the latter is more firmly retained and can only be driven off by calcination.

When soda is heated it melts at a low temperature and forms a watery flux which continues to evolve aqueous vapour until the whole of the water of crystallisation has evaporated It is only when greater heat (strong red heat) is applied that the residual water is driven off and the soda is converted into anhydrous sodium carbonate, which is commercially known as "calcined soda"

As the anhydrous form will absorb water when brought into contact therewith, and change into soda crystals, which dissolve in the water, calcined soda can be used for purposes for which a solution of soda is required, and is often purchased, in preference to the crystals, in order to save expense of dead freight on the water of crystallisation

For enamel manufacturers, of course, water is a useless encumbrance; and they, therefore, buy calcined soda exclusively. As, however, the ordinary calcined soda, even when perfectly white in appearance, always contains a notable proportion of iron compounds which spoil the colour of enamel by producing a yellow tinge, this soda can only be used for enamels wherein colour is an unimportant consideration

Enamel Soda.

The trade in soda for enamel-making having developed considerably, alkali makers now comply with the demand for a non-ferruginous soda and supply, under the name of "enamel soda," a product which may be regarded as perfectly free from iron. To this end the soda is purified by frequent crystallisations until the most delicate reagents fail to reveal the presence of iron, except in traces, the product being afterwards spread out in heated rooms until thoroughly dry.

Enamel soda is, it is true, dearer than the ordinary kind; but it furnishes a pure white enamel, whereas the ordinary soda, even when fairly pure, gives rise to a yellowish tinge, the extent of which depends on the amount of iron present.

Kelp.

This article of commerce is an impure soda obtained by calcining seaweed on the Irish and Scottish coasts As it contains a number of other salts in addition to sodium carbonate it is unsuitable for any but the commoner kinds of enamel. Since the development of the manufacture of soda from common salt, the trade in this impure soda has greatly declined.

Glauber Salt (Sodium Sulphate).

At present this salt is obtained in large quantities as a by-product in the manufacture of nitric acid, and usually occurs in the form of white hemispherical cakes, in which condition it is recovered on breaking the glass retorts used for distilling the nitric acid (from sodium nitrate and sulphuric acid). This kind of Glauber salt is less contaminated with extraneous bodies than the other qualities obtained when crude nitric acid is prepared by distillation in iron cylinders.

In the first stage of soda manufacture, common salt is converted into Glauber salt and hydrochloric acid, by treatment with sulphuric acid The product in this case is rendered very impure by iron compounds and would furnish yellow enamels, consequently it must be purified by repeated recrystallisations from solution in water, followed by dehydration.

Pan Stone

Is usually a mixture of sodium and calcium sulphate, but always contains, in addition, a certain quantity of substances capable of colouring glass, and therefore is unsuitable for the production of fine enamels.

ALKALINE EARTHS

The substances classified under this title, although exhibiting strong basic properties and in this respect resembling the alkalies, differ from the last named in being only very sparingly soluble in water and in forming insoluble compounds when fused with silica. For our purposes only two of the alkaline earths come under consideration, *viz.*, lime and magnesia

Lime (Calcium Oxide).

Lime does not occur in a pure state in nature, but is found in enormous quantities in the form of calcium carbonate (limestone, marble, chalk, etc.), and calcium sulphate (gypsum, alabaster). The carbonate is the usual variety employed in making glass and enamel

Limestone.

Ordinary limestone is composed of calcium carbonate, and almost invariably contains foreign admixtures capable of exerting an injurious influence. Most limestones contain small quantities of organic matter, ferrous carbonate, magnesium carbonate and occasionally clay as well.

Organic matter, unless in excessive amount, is not harmful, the carbon formed therefrom in the process of smelting being capable of removal by the addition of small quantities of oxidising substances. If, however, the proportion of organic matter is so large as to render the limestone dark grey or black, the latter is hardly fit for use as a constituent of enamel, unless previously treated, for which purpose the limestone may be advantageously burnt in kilns, an operation resulting in the elimination of both the carbon dioxide and the organic matter.

More ominous is the presence of ferrous carbonate as a constituent of limestone, since even small quantities of this salt will impart a noticeable bottle-green coloration to enamel. Ferric oxide has a less powerful influence on the colour than ferrous oxide, consequently, in testing the suitability of a limestone for the manufacture of enamel, it is advisable to make a small trial smelting, with an addition of some oxidising agent, to convert the ferrous oxide into ferric oxide, which latter will tinge the glass yellow, but less powerfully than the ferrous oxide would colour it green.

Furthermore, the suitability of a limestone for our purpose can be gauged by its appearance after prolonged exposure to the air, a reddish-yellow coloration of the lumps, or the formation of a number of red veins therein, indicating the presence of iron in large proportion; such a limestone may be rejected as unsuitable, without any further test.

Dolomite.

Many limestones, and more particularly the so-called dolomites, contain variable quantities of magnesium carbonate. The effect of this compound is to cause the enamel to become more refractory in direct proportion to the amount of magnesium present; in some cases this property is beneficial. As far as colour is concerned, magnesia has no influence at all —the silicates of the metal being themselves colourless

Chalk.

Chemically speaking, the pulverulent white mineral, chalk, consists of calcium carbonate. Examined under the microscope, it is seen to be made up of the shells of tiny marine animals, the organic matter of which has, however, long disappeared. For our purposes chalk is an excellent material, since it is free from iron, and, being in an extremely fine state of division, readily unites with the other ingredients during the operation of smelting

Calcined mussel shells also constitute a splendid material for enamel-making, wherever they are obtainable in large quantities, as they consist of nothing but very pure calcium carbonate.

Argillaceous Limestone

Certain limestones, known under the name of marl, contain large proportions of clay and are also generally rather rich in iron. Even apart from the latter consideration, such limestones cannot be recommended as raw material for enamels, the presence of clay rendering the product very refractory. Moreover, the amount of the clay and its behaviour can only be accurately determined by chemical analysis and trial smeltings respectively.

Causticising Waste (*Kalkascher*).

Where wood ashes are converted into caustic lye, for soap-making, by treatment with slaked lime and lixiviation in large tubs, a residue is obtained, consisting for the most part of calcium carbonate together with a small amount of potash salts, and almost all the ferric oxide present in the wood ashes. In point of quality this product is comparable with ferruginous limestone and is therefore of but very low value as a material for the preparation of enamel.

Magnesia.

This alkaline earth, which resembles lime but is more sparingly soluble, occurs in nature as magnesium carbonate (magnesite), and magnesium sulphate (Epsom salts), and as already stated, dolomite consists of varying proportions of the carbonates of lime and magnesia. Magnesium carbonate is also met with as a manufactured product in commerce.

Magnesium Carbonate.

Small quantities of this salt are used in the manufacture of enamels, to reduce their fusibility, and freedom from iron is a particularly important consideration. Good magnesium carbonate must form a pure white, very light mass, that can be easily reduced to an impalpable powder by rubbing between the fingers.

Magnesium Sulphate (*Epsom Salts*).

This substance appears in the form of colourless, readily soluble crystals of very bitter taste, and parting with their water of crystallisation when heated. It is not very often used in the preparation of enamels.

Lead Compounds

The silicates of lead being colourless and readily fusible, compounds of this metal are frequently employed for producing fusible enamels, the most common forms being the oxides (litharge and red lead) or the carbonate (white lead).

Lead Oxide.

Lead oxide is met with in commerce as a product of certain smelting works, and especially as a by-product of the refining of silver lead There are two principal qualities—massicot and litharge, the former being the handsomer, and forming by reason of its fine yellow shade a good artist's colour, it is however too dear for enamels.

Litharge differs from massicot by its inferior pale yellow colour, and is to be had at much lower rates It is usually a by-product of the preparation of silver from silver lead.

Since, however, this kind of lead occasionally contains iron and copper, which pass into the litharge as oxides, it is impossible to produce white enamels from such impure raw material, the latter must therefore be examined by analysis or by a trial smelting The green coloration noticeable in certain parts of the litharge indicates, of itself, the presence of copper.

When purchasable, litharge made from very pure lead (*e.g*, Carynthian litharge), is exceedingly well adapted for our purpose A very small percentage of foreign metallic oxides may be present without any ill effect on the quality of the enamel, but practical experience has shown that the proportion of the various metals in litharge should not exceed :—

Copper	0 0041	per cent
Antimony	0 0050	,,
Bismuth	0·0050-0 0075	,,

if perfectly white enamels are to be made

As already mentioned, particular care in the selection of materials is only necessary when a perfectly white or pure-coloured product is desired, whilst in the case of technical enamels the principal point to be considered is the adjustment of the constituents so as to yield a durable article.

Red Lead (Minium).

This is also an oxide of lead, but differs from litharge (PbO) in containing a larger proportion of oxygen, its composition being represented by Pb_3O_4 or Pb_4O_5. It is prepared in red lead works, by roasting finely powdered litharge, and, when a certain temperature is reached, acquires the fiery red colour on account of which it is employed by painters.

So far as the colour of red lead is concerned, this is quite immaterial for our purpose, and the only reason why enamel-makers should prefer to have it as brilliant as possible, is that this condition is an indication of purity and freedom from iron or copper, since it is only from litharge that is excellent in this particular that a really good coloured red lead can be obtained.

During the fusion of the enamel mass, red lead gives off oxygen and is reduced to the state of PbO which combines with silica. The liberated oxygen converts any ferrous oxide present into the ferric state and also facilitates the combustion of the last traces of organic matter in the quartz sand. Though somewhat expensive, red lead is an excellent material to use in making enamel on account of the above-mentioned properties.

White Lead

White lead (basic lead carbonate) is made on a large scale in special factories, for use as a paint. In the pure state it is a brilliant white, amorphous powder, and it is on account of its non-crystalline nature that this body possesses such extensive covering power as a pigment. For the purposes to which white lead is devoted in the manufacture of enamel, however, this property is of no value, and therefore the cheaper crystalline variety will do equally well. The principal consideration is perfect freedom from iron, copper, or other impurities, and as the commercial grades are frequently adulterated with large quantities of finely ground barytes, clay and other heavy substances, for the sake of cheapness, such kinds are absolutely worthless for our purpose, and, indeed, are capable of injuring the properties of the enamel. Consequently none but perfectly pure white lead should be purchased. Fortunately this can be done, as all large makers will supply it of guaranteed purity; besides, adulteration can be detected in a very simple manner as follows —

Pure white lead will dissolve completely, without leaving any residue, in dilute acetic acid, the presence of residue indicating adulteration with barytes, clay, or gypsum. To test for chalk, the solution of white lead in the above acid is treated with a current of sulphuretted hydrogen gas so long as a precipitate of lead sulphide continues to form, this latter is then separated by filtration, and the filtrate is treated with ammonium oxalate solution The occurrence of a white precipitate shows that the white lead contained chalk.

In itself, the presence of such chalk is not adverse to our purpose, since lime is a constituent of enamel; but there is no need to pay for chalk at the high rate charged for white lead, and therefore it is well to test the sample and assure oneself of its purity or otherwise.

Lead Sulphate.

This salt is recovered in large quantities as a by-product in many chemical processes, and can be bought at a low price.

For our purposes it possesses the admirable property of being perfectly free from iron and copper, and is as suitable as any other lead salt for the manufacture of glass and enamel. To reduce this sulphate a little carbon is added to the mass before smelting—as must also be done when other sulphates (*e.g.*, Glauber salt or magnesium sulphate) are used

BARYTES (BARIUM SULPHATE).

This is another material to which attention should be directed as suitable for use in enamel manufacture, especially on the large scale. It occurs naturally in many places, as the so-called heavy spar; and is, in point of chemical composition, barium sulphate. As it belongs to the alkaline-earth group, barytes may be employed for our purpose to replace a portion of the lime used.

Properly constituted enamel masses containing barytes must also contain lime, in addition to soda, and will then yield very useful products. According to Benrath a baryta glass, having the following composition :—

$$4\ Na_2O + 4\ BaO + 4\ CaO_2 + 36\ SiO_2,$$

exhibits the properties of a good lead glass, and is more readily fusible than ordinary glasses, but, unlike lead glass, is not attacked by a reducing fire.

Witherite.

This mineral consists of barium carbonate and can be used in place of heavy spar. When the latter is employed an addition of carbon is requisite in order to reduce the sulphate but this is unnecessary in the case of witherite.

IV.

SUBSTANCES ADDED TO PRODUCE OPACITY.

The materials described in the previous section are those forming the true glass substance. Other bodies have also been proposed, as zinc oxide, by whose aid glasses suitable for certain purposes can be prepared, though it is not advisable to resort to such bodies in compounding enamel masses.

Enamels always contain certain infusible white substances which render the glass opaque, and for this purpose, as already mentioned, use is generally made of tin oxide or bone ash. In view of the great influence exerted by these two materials on the character of the enamel, a fuller description of them must now be given

TIN OXIDE (STANNIC OXIDE).

Tin oxide (SnO_2), when chemically pure, is a heavy powder of a pure white colour, and by itself is totally infusible. When suspended in a finely divided condition in, and enveloped by, a fused colourless mass (glass) it renders the latter translucent or altogether opaque, according to the proportion in which it is used.

In commerce this oxide is met with as so-called "tin ash"; but as this is never quite pure and always contains lead oxide, frequently associated with ferric oxide and small quantities of cupric oxide, it is advisable to prepare one's own tin oxide either by the wet or dry process.

In the wet process, fine tin is first granulated by melting the metal and pouring it into cold water. This is then shaken up with fuming nitric acid in a vessel of glass or glazed porcelain, whereupon a brisk reaction occurs, the nitric acid being decomposed, with evolution of brown fumes, whilst the tin is converted into a white powder—tin oxide—which settles down to the bottom of the vessel. As soon as the action of the nitric acid has abated, a fresh quantity is added, and is followed by further gradual additions until finally the reaction ceases altogether

Owing to the violence of the reaction the acid must be added in small quantities at a time, as otherwise the contents of the vessel will come over; the work should also be done in the open air or under a chimney with a good draught, as the brown fumes (nitric oxide and hyponitrous acid) cause great inconvenience to the respiratory organs.

After the reaction is at an end, the vessel is left at rest for a day, whereupon the supernatant acid (which may be used over again) is carefully decanted from the white deposit, and the latter is washed several times with water, by sedimentation To remove the final traces of nitric acid, the tin oxide precipitate is afterwards repeatedly washed in a glass funnel and then dried, the funnel being meanwhile kept covered over with paper to exclude dust

The product thus obtained is of excellent quality, but is too expensive for any but the finest enamels, which are required to remain perfectly white or be tinged with very delicate colours.

To prepare tin oxide by the dry method, the process employed by manufacturers of tin ash is imitated, the metal being fused in a flat stoneware pan and afterwards raised to a strong red heat. The rapidity of the oxidation is in direct proportion to the temperature to which the molten metal is exposed.

At first the surface of the metal becomes covered with a blackish pellicle, consisting of tin protoxide (stannous oxide), but when more heat is applied this is converted into stannic oxide, a change indicated by the whitening of the pellicle. This skin is now removed by means of a hook, whereupon the underlying surface of metal forms another pellicle of oxide directly it comes into contact with the air. When the temperature is sufficiently high, the process of oxidation goes on very rapidly, so that a large quantity of tin can be converted into oxide in a short time.

The operation may also be accelerated by employing an alloy of tin and lead, the following proportions —

Tin	82 per cent
Lead	18 ,,

being highly adapted for the purpose. Of course the amount of lead present must be borne in mind when compounding the enamel mass, and the amount of lead oxide be proportionally reduced. An alloy of the foregoing composition oxidises more readily than pure tin, and furnishes a yellow-looking mass, the colour of which is due to the lead oxide present. When the enamel mass is fused, the lead compound combines with silica and the pure tin oxide renders the product opaque.

Crude tin ash always contains a certain amount of unaltered tin and stannous oxide. The simplest method of eliminating these impurities is by moistening the mass with fuming nitric acid and leaving it to stand for a while, the action of the acid being to convert both substances into stannic oxide. This method, however, is applicable only when pure tin has been employed, as in the case of tin-lead alloys—the nitric acid dissolves the resulting lead oxide.

In the latter event, therefore, the product must be purified by sedimental washing (elutriation), by which treatment the particles of metal are left behind; the final traces of stannous oxide in the product are then converted into stannic oxide by calcining the dried mass in thin layers.

BONE ASH.

In the case of enamels which are merely required to be translucent, without being brilliantly white, bone ash may be used with advantage. This substance, prepared by calcining bones in presence of air and then grinding and elutriating the residue, forms a greyish-white powder, and chiefly consists of tri-basic calcium phosphate together with calcium and magnesium phosphate

For our purpose the calcium phosphate is the principle constituent, which substance, when pure, is a perfectly infusible white crystalline mass A large proportion of the bone ash now met with in commerce comes from South America, the meat extract factories at Fray-Bentos in Uruguay employing the bones of the slaughtered cattle for heating the furnaces. Bone ash of dark grey colour contains an admixture of carbon from the added fuel, but this substance can easily be got rid of by adding to the enamel mass a little saltpetre, which, during the process of smelting, gives off oxygen and consumes the carbon.

SUBSIDIARY INGREDIENTS.

This category comprises all substances added to the white fundamental mass of the enamel with the object of modifying its properties in any way. They may be subdivided into three classes according to the purposes which they are intended to serve :—

1. *Fluxes*, to increase or diminish the fusibility of the mass.
2. *Pigments*, to colour the enamel
3. *Decolorants*, for modifying or totally destroying the colour of the fundamental mass.

V

FLUXES.

The attainment of a suitable degree of fluidity in an enamel at a given temperature, is one of the most important factors in the operation of enamelling, and depends greatly on the skill of the operator entrusted with the duty of mixing the ingredients to be melted

As, in almost every factory where enamels are prepared on a large scale, certain proportions are adhered to in mixing, whereby the composition of the raw materials at disposal has to be taken into consideration, the nature and quantity of the fluxes to be used can only be ascertained by special experiments in each case, and for readily apparent reasons, the makers usually keep their formulæ secret

We can therefore only deal with the properties of the fluxes in a general manner, reserving more exact particulars as to the amounts to be used in order to produce enamels of definite character, until the section devoted to formulæ is reached, such recipes being calculated on the basis of perfectly pure materials. The fluxes used in the enamel industry are: borax, fluor spar, clay, broken glass (cullet), porcelain sherds, gypsum and felspar

BORAX.

This substance, which forms one of the most extensively employed fluxes in nearly all enamel works, behaves in a peculiar manner, in that it plays a direct part in the formation of the glass matrix. Before passing to the influence of borax on the character of enamel, we will first devote a little attention to the chemical properties of this salt.

In point of chemical composition borax is a compound of sodium, boron and oxygen, *viz.*: sodium biborate ($Na_2B_4O_7 + 10H_2O$), and forms prismatic crystals which dissolve in twelve parts of cold, or two parts of hot, water. In addition to this ordinary form a second variety is known under the name of octahedral borax, differing from the former by containing only half as much water of crystallisation.

When heated, borax fuses at a moderate temperature and very soon begins to froth up (intumesce) to such an extent that a very large vessel must be employed or the mass will overflow. In this process, water of crystallisation is given off, and finally, a white, highly porous residue of calcined borax is left.

For the purposes of the enamel-maker calcined borax is generally used, the frothing of the ordinary kind being a source of great trouble in the melting process. While still warm, the calcined borax is reduced to fine powder and stored in properly closed vessels; otherwise it greedily absorbs moisture from the air and changes back—at least in part—into the crystalline form.

When calcined borax is heated to bright redness it finally fuses into a colourless glassy mass, the so-called vitrified borax, or borax glass. For our purposes, however, this treatment is unnecessary, the same result being produced in the melting of the enamel.

It is, however, always advisable to melt a small sample of the borax before purchasing, in order to test for the presence of pigmentary oxides. If pure, the borax will remain as clear as glass, but if the fused mass exhibits a yellow tinge ferric oxide is indicated; copper gives a green coloration, and manganese compounds a violet shade.

From a chemical point of view the behaviour of borax resembles that of silica to a certain extent. It consists as already stated of sodium biborate (acid borate)—that is to say, the boric acid present is only half saturated and is still able to combine with metallic oxides. Now, boric acid exhibits many points of similarity to silica in that, while only a weak acid, at the ordinary temperature, its fire-resisting properties enable it to displace the strongest acids from their combinations, at red heat

Of the salts formed by boric acid, only those of the alkalies are soluble in water, and the fusion of an insoluble borate with a soluble one results in the latter being also rendered insoluble Thus, for example, when sodium borate and calcium borate are fused together in certain proportions, the resulting mass looks like a colourless glass and may be regarded as such a one in which silica is replaced by boric acid.

When a basic oxide is brought into contact with borax a double salt is formed, the second equivalent of boric acid combining with the oxide in question whilst the salt thus formed unites with the neutral sodium monoborate As a rule, however, glasses containing boric acid alone, are not prepared, but only a portion of the silica is replaced by boric acid in compounding glass and enamels

The most valuable property of boric acid glasses, for our purpose, is that they usually have a fusing point much lower than that of silica glass, and will run freely at a temperature whereat the latter is still semi-fluid. It must, however, be noted that the resisting power of enamels and glasses containing boric acid is inferior to those containing silica alone.

The addition of lead oxide and borax to an enamel mass gives an enamel characterised by a very low fusing point, and consequently one that can be used in very thin layers. No only, however, does the use of borax depend on this property, but it also serves a very important purpose in the preparation of coloured enamels, namely, to dissolve the pigmentary metallic oxides, and as the borates of many heavy metals form highly characteristic and handsomely coloured compounds borax is added to the mass with this object in view. Besides, the fluidity of the enamel mass, when borax is present, facilitates the uniform distribution of the colour.

The tints imparted to borax by certain of the metallic oxides are so intense that, as already mentioned, this salt is employed as a blowpipe test for small traces of those metals; and this property is of special value to the enamel-maker as affording a simple means of detecting impurities in his raw materials. This matter will be referred to later on.

BORIC ACID.

We have already seen that the active substance in borax is the semi-combined boric acid, and this acid in the free state can, under certain conditions, be used direct instead of the sodium salt. At the present time boric acid can be obtained pure, in commerce, in the form of pearly, and somewhat greasy-feeling, crystalline plates.

When added to an enamel mass, boric acid behaves in a similar manner to borax, in such event care must be taken to make up for the deficiency as regards soda in the mass; as, however, this requires special calculation, enamel manufacturers generally prefer to use calcined borax and leave boric acid alone.

FLUOR SPAR.

Fluor spar or fluorite is a mineral composed of calcium and fluorine (CaF_2), and occurs in nature either as handsome tessular crystals or in compact masses. It may be perfectly water-white in appearance, but other specimens exhibit a variety of colour in many different shades. Since these colorations are due to the presence of small amounts of metallic oxides, it is always preferable for our purpose to employ the colourless or only slightly tinged kinds.

Used alone, fluor spar fuses at a red heat and consequently diminishes the refractory character of enamel masses. It should, however, be observed that when the mass contains an excess of silica, uncombined with bases, this body decomposes the fluor spar during the process of fusion—calcium silicate being formed

CLAY.

The mineral to which the general name of clay has been given exhibits highly divergent characteristics, which are due to the conditions under which the clay was formed Now clay is a product of the decomposition of felspar, which latter body consists of silicates of aluminium and potash, and therefore resembles glass in composition Under the destructive influence of air and water, felspar is decomposed, the aluminium silicate remaining behind as an insoluble substance —clay, whilst the potassium silicate is carried away by the water. Hence it is that crystals of felspar are not infrequently found coated with aluminium silicate

KAOLIN, OR PORCELAIN EARTH.

Porcelain earth (*Chinese*, kaolin) may be regarded as the purest form of clay, and consists exclusively of aluminium silicate. It forms an insoluble, pure white powder, infusible at the highest furnace temperature attainable; and therefore may be used for the same purpose as tin oxide or bone ash, namely, to impart a white colour to glass To some extent porcelain may be considered as a glass, which melts only at the highest temperatures attainable in our furnaces, and consists of felspar and silica containing very finely divided particles of kaolin in suspension, so that, in thin pieces, porcelain is translucent, but perfectly white in thicker layers.

If, however, kaolin is fused along with mixtures containing silica in excess, it is partly dissolved and forms with the silica an unusually refractory glass. Hence kaolin is used for this purpose in the manufacture of enamel; great care being, however, necessary in apportioning the amount of kaolin added, since the enamel mass may thereby easily be rendered so refractory as to be practically infusible, especially in large quantity.

WHITE, OR PIPE, CLAY.

This kind of clay is a kaolin more or less contaminated with lime and quartz sand, in consequence of which it fuses at a much lower temperature than porcelain earth; though, like the latter, it is used to diminish the fusibility of enamel masses. Both kinds of clay should be entirely, or very nearly, free from traces of iron oxide, or undesirable colorations of the mass will ensue.

In fact these two clays are really the only ones at all suitable for the purposes of the enamel-maker, the other varieties being usually so highly contaminated with other minerals as to yield only coloured enamel masses. Clays formed by the weathering of felspathic rocks (granite, gneiss) frequently contain a deal of mica, the ferrous oxide in which colours the enamel green; others again are so charged with ferrous oxide as to appear of a grey-blue colour, which, when the clay is calcined, changes into the well-known brick red, owing to the conversion of the ferrous oxide into ferric oxide; whilst still other clays contain so much lime and quartz sand that they sinter, or even melt, in the heat of the brick kiln, and change into a blackish vitreous mass. Clay exhibiting this tendency is of little value to the enamel-maker, and is, at the most, only suitable for common dark coloured qualities.

FELSPAR.

This mineral is met with in a variety of forms in nature: sometimes alone, sometimes as a constituent of rocks, like granite, gneiss, etc.

In composition, ordinary felspar is a combination of aluminium silicate with potassium silicate. For our purposes the white kind, known as albite, is the chief one to be considered, the coloured varieties being less suitable owing to their content of ferric oxide.

Pure felspar fuses only at the temperature of the porcelain kiln, and then forms a transparent, highly crystalline mass of considerable hardness. As already mentioned, it constitutes in conjunction with silica the true matrix of porcelain within which the kaolin particles are embedded. The addition of felspar to enamels greatly decreases their fusibility.

By reason of its hardness, felspar has to be prepared in the same manner as quartz, *viz.*, by quenching, in order to obtain it in a finely-divided condition.

GYPSUM

Gypsum, which is calcium sulphate in combination with water, is found in a high state of purity, in crystalline masses (moonstone), or fine-grained (alabaster, gypsum), all these kinds being suitable for our purposes, except greyish-blue and red gypsum, the colour of which is due to oxides of iron.

As a general thing, in the preparation of enamels, gypsum is used only in conjunction with felspar or barytes, its effect on the refractory properties of enamel is to reduce them to a moderate extent.

PORCELAIN SHERDS.

As porcelain usually consists of felspar, quartz and kaolin, the first and last of these substances when added to enamel in the form of ground porcelain sherds, render the product more refractory, while at the same time its power of resisting the action of chemicals is also increased. In sorting out the porcelain sherds for enamel, all painted pieces must be thrown out, as otherwise they would impart colour to the product.

BROKEN GLASS (CULLET).

Glass constituting the matrix of enamel, the addition of glass cullet to the enamel mass is therefore a rational proceeding. Owing to the considerable variety in the composition of different kinds of glass, however, it is always necessary to determine beforehand, by a trial smelting, the amount and nature of the additions to be made to the glass to produce an enamel mass of suitable character.

The sorting of the cullet is an important operation, as, for white enamel, all coloured glass must be excluded and only plain glass used. The coloured pieces are collected and smelted by themselves for use in lower class goods where colour is of less importance. If the glass is too fusible, this defect can be remedied by an addition of refractory substances, while in the converse event fluor spar, etc., may be added.

Owing to the great differences in composition and fusibility of the various kinds of glass, it is only by experiment that the remedies to be employed can be ascertained.

VI

PIGMENTS

Enamel masses have the property of acquiring any desired colour, and, when properly prepared, the colours are characterised by brilliancy, lustre and indestructibility—qualities which explain the preference shown for coloured enamels in the production of very valuable works of art.

Although, in the case of enamels for technical purposes, colour is a minor consideration in comparison with the inner qualities of the product, *viz.*, power of withstanding the action of chemicals and considerable fluctuations of temperature, beauty of colour is nevertheless a matter of some importance even in such enamels. Thus it is well known that cooking utensils, for example, that are coated with nicely coloured enamels, have a better sale than those covered with white enamel, notwithstanding that the latter is much more serviceable than the others.

The pigments employed in this industry are all of the metallic-oxide group. As already mentioned, certain oxides of the heavy metals have the property of colouring glass; and though very highly coloured glasses are used to colour certain enamels, it must be remembered that the pigmentary principle of these glasses is an oxide, and consequently one is justified in saying that the colour of all enamel masses is due to certain metallic oxides.

The object of the present work is twofold, in that it is intended to treat of the preparation of enamel masses both for artistic and industrial purposes. The technical man, who is occupied with the manufacture of large enamelled articles, is principally interested in the inherent qualities of certain enamel compositions; whilst the artist or the maker of artistic objects chiefly looks at purity and delicacy of colour.

Keeping the latter circumstance in view, we must therefore treat the study of pigments—so far as it concerns our purposes—in a more exhaustive manner; and also because, in the author's experience, the market for chemical preparations of this nature is only badly supplied, many of the so-called pure pigments met with in commerce belying their name, and being therefore incapable of furnishing pure shades of colour.

While it is true that some chemical manufacturers supply the pigments required for enamel in a sufficiently pure condition, the prices are mostly so high that it is preferable to make the pigments oneself. Usually the manufacture of chemical preparations necessitates an accurate knowledge of chemistry; but as the substances required for colouring enamels are most frequently used by artists and makers of artistic products who are seldom possessed of an extensive acquaintance with that science, the description, given in the following pages, of the methods of preparing the pigments in question, will be of such a nature as to enable those whose chemical knowledge is merely slight to make the substances they require.

The pigments used for enamel masses are as follow:—

For yellow: antimony oxide, potassium antimonate, potassium antimonite, lead antimonate, silver oxide, ferric oxide, uranium oxide.

For red: ferric aluminate, sodium-gold chloride, tin-gold chloride, purple of Cassius

For orange: mixtures of pigments for yellow and red.

For green. cupric oxide, chromic oxide, or ferrous oxide.
For blue · cobaltous oxide, cobalt silicate or smalt zaffre.
For violet manganese oxide.
For brown ferric oxide.
For black ferrous oxide in large proportion.

The above list mentions only the principal fundamental colours obtainable by the aid of the pigments specified. These colours are, however, insufficient by far for the purposes of painting in enamel, the artist in this branch requiring as large a range of colours as his other *confrères* of the brush in order to be able to obtain any desired shade. Now, the latter object can only be attained by employing larger or smaller proportions of the pigmentary materials, and thereby producing a graduated scale of shades of the pure colours, and when it is desired to have mixed colours the chemical composition of the pigments will have to be modified in certain ways, or special artifices must be resorted to.

As a more suitable opportunity of considering the latter eventualities will arise when the process of enamelling is under discussion—the matter may be left over until then, and attention now directed to the purely chemical side of the question, namely, the preparation of the various pigments, not omitting to mention that the use of chemically pure materials enables one to obtain any desired shade much more easily than when special attention has to be bestowed on the presence of impurities accompanying the true active principles in the pigments employed

YELLOW PIGMENTS

The sole means of producing a pure yellow in enamels is by the aid of antimony oxide, potassium antimonite or silver oxide; for cheaper qualities, however, ferric oxide is also used, though, strictly speaking, the colour obtained is not yellow at all, but a peculiar reddish brown, such as may be seen in an intense form in brown wine bottles.

Antimony Oxide.

This oxide may be prepared by the wet or dry method. In the former case, finely powdered metallic antimony is placed in a glass vessel (standing in a basin of water) and treated with nitric acid of a certain strength. The acid rapidly attacks the metal and converts it into a white powder, reddish-brown fumes being evolved. Owing to the violence of the reaction, the acid must be added in small quantities at a time or the contents of the flask will overflow, even when the latter is comparatively large. Towards the close, the reaction abates and may then be assisted by carefully heating the water bath in which the flask is immersed.

To obtain a product of well-defined properties it is necessary to work precisely in accordance with the instructions now given. The following quantities, *viz* :—

Powdered antimony .	1 part by weight.
Nitric acid (sp gr. 1.2) . .	4 parts ,, ,,
Water	8 ,, ,, ,,

are taken, and the ensuing product (the *Stibium oxydatum grisum* of the pharmacist) must be thoroughly washed with hot water and weighed, it is, however, not quite pure, as it always contains small quantities of unaltered metal and basic antimony nitrate. Nevertheless, as the proportion of these impurities will always be constant, provided the above conditions are adhered to in making the preparation, it will be easy, by means of a few tests, to produce well-defined shades of yellow with this material. The washing in hot water is an important feature, and must be continued until the liquid ceases to take up any portion of the precipitate into solution.

When metallic antimony is heated in an inclined crucible it quickly fuses and, when the heat is increased, takes fire, this effect being accelerated by blowing air into the crucible. The combustion is accompanied by a peculiar bluish flame and dense white fumes of antimony oxide are given off. These condense on the cooler upper sides of the crucible—which therefore should not be embedded in carbon—and form delicate lustrous needles, which are scraped off and removed from time to time.

This oxide (*Flores antimonii argentei*, or *Nix stibii*) is also impure and usually contains variable proportions of antimonic acid and antimony antimonate. To restrict the formation of the latter it is advisable to heat the crucible no higher than is necessary to cause the antimony to ignite and continue burning.

A better method than the foregoing is to raise a crucible to strong red by embedding it in glowing charcoal, and throw in small quantities of the following finely powdered and intimately mixed ingredients:

Antimony	37 parts by weight.
Saltpetre	20 ,, ,, ,,
Potassium bisulphate	15 ,, ,, ,,

When the whole has been thrown in, the crucible is kept red hot until the contents flow calmly, whereupon they are poured out on to a cold stone slab. On breaking up the solidified mass and extracting it with boiling water, nearly pure antimony oxide is left.

The purest oxide, and that most suitable for fine enamels is obtained as follows.—

Commercial antimony sulphide is reduced to fine powder and boiled in a glass or porcelain vessel with hydrochloric acid, in which it dissolves with evolution of sulphuretted hydrogen. When perfectly cold the liquid is decanted from the insoluble residue and transferred to a large vessel containing at least a twenty-fold quantity of water, into which the solution is run as a thin stream with continual stirring. The entire liquid immediately turns milky white, and a heavy white powder (powder of algaroth) is precipitated. This is collected in a conical filter of closely woven linen and washed with water, after which it is placed in a basin and suffused with a solution of 1 part of soda crystals in 3 parts of water, the amount of this solution being such that even after prolonged standing, subsequent to boiling, it still remains alkaline to test-paper. The contents of the basin are again placed on a linen filter, thoroughly washed with water, dried, and stored in a closed vessel. The product is chemically pure antimony oxide.

Potassium Antimonite.

This preparation, which furnishes an inferior yellow to that yielded by pure antimony oxide, is obtained by mixing commercial antimony sulphide with half its weight of saltpetre, and throwing the mixture in successive small quantities into a red-hot crucible, which is then heated for some time longer and set aside to cool. On breaking the crucible a white fused mass is found, underneath which is generally a layer of unaltered, fused antimony sulphide. The white mass is finely powdered dry, and stored, it consists of potassium antimonite, together with a little potassium sulphate and potassium antimonate, and is suitable for preparing commoner grades of yellow. In point of beauty of colour, however, the chemically pure antimony oxide prepared from antimony sulphide and hydrochloric acid by the wet method, is superior to any other preparation of antimony.

When fused with enamels, antimony preparations yield a specific yellow which may be toned by adding suitable adjuncts; thus, an addition of red lead produces Naples yellow, while with ferric oxide an orange yellow is formed. The reaction occurring during the fusion of the enamel mass in presence of red lead is of the following nature:—

At red heat, minium (red lead) gives off oxygen, and is reduced to the state of litharge, the liberated oxygen instantly oxidising the potassium antimonite and producing antimonic acid, which unites with the litharge, whilst the potash combines with silica. As a matter of fact, the reaction does not go on so smoothly as this in practice, and considerable experience is necessary to hit off the exact shade required, by adding red lead. It is therefore advisable to make use of the lead antimonate in a ready-made condition, which may be prepared by the enamel-maker, as the commercial Naples yellow is expensive to buy.

Lead Antimonate (Naples Yellow)

The simplest method of preparing this pigment is by intimately mixing 1 part of chemically pure tartar emetic with 2 parts of lead nitrate and 4 parts of common salt (sodium chloride), and fusing the mixture in a Hessian crucible at a moderate red heat. This done, the contents of the crucible are poured into a deep vessel of water, the crucible itself being also dropped in when cold; common salt passes into solution and lead antimonate is left behind as a yellow powder. The object of adding the sodium chloride is to prevent the temperature rising beyond a certain limit (the point of volatility of this substance) during the operation of fusion.

The smelting of the mixture requires, however, a certain amount of care to maintain the most favourable temperature. Thus, if the mass is heated just to fusing point, the resulting pigment will yield an orange shade, while the more it is heated the nearer will the colour approach lemon or sulphur yellow, and the mass when poured into water will be hard, requiring to be broken up and extracted with hot water.

A very handsome Naples yellow can also be prepared by fusing 2 parts of tartar emetic with 8 parts of common salt and 4 parts of lead nitrate. The fused mass is treated in the cold with dilute hydrochloric acid which dissolves out the excess of lead oxide and leaves a deep coloured pigment.

Silver Oxide.

An unusually handsome but expensive yellow for enamels can be obtained by the use of silver oxide. Here, however, a chemically pure oxide is essential, and such may be prepared in the following manner:—

Commercial silver is dissolved in nitric acid, the solution being blue from the copper accompanying the silver. Hydrochloric acid is then added so long as the caseous precipitate of silver chloride continues to form. This is filtered off and washed with water until the washings no longer turn blue on the addition of ammonia. When this is the case the precipitate on the filter consists entirely of chemically pure silver chloride, which, when dried, is ready for use. This preparation is, however, more difficult to work with than silver oxide, and it is therefore advisable to convert the chloride into oxide, by placing the undried salt in a large glass vessel along with strips of zinc, and water strongly acidified with hydrochloric acid. In a very short time the white silver chloride begins to turn black and is reduced to the metallic state, as a greyish-black powder in an extremely fine state of division.

When the reaction is terminated the silver is collected on a filter, thoroughly washed with water, and dissolved in nitric acid, from which solution it is thrown down again, by caustic potash, as hydrated silver oxide, which is then collected and dried. An enamel containing silver oxide, exhibits, after fusion, a superficial coating of metallic silver, resulting from the reduction of the oxide, but when this is scraped off with a sharp tool a beautiful and intense yellow is disclosed. The colour can also be produced by mixing dry silver chloride with the enamel, but in this case the attainment of the exact shade is more difficult than when the oxide is used.

Ferric Oxide

In concluding the description of the yellow-producing pigments, mention should be made of ferric oxide. This substance, when used by itself, furnishes the well-known yellowish red-brown colour to be seen in brown wine bottles, but when mixed with other pigments produces a corresponding modification of tone. When added in large proportion it turns enamels quite black

Owing to its low price, ferric oxide is largely employed as a pigment for enamels, and is generally used in the form of commercial colcothar (*Caput mortuum*), which, however, is never quite pure, and consequently does not furnish bright colours

To obtain a perfectly pure oxide, suitable for producing shades ranging from pale yellow to bottle brown, the following method may be pursued

Iron, of a very pure kind (*e g*, shoe nails), is treated with dilute sulphuric acid in which it dissolves, with evolution of hydrogen The solution is filtered, and, after being heated to boiling, is treated with potassium oxalate solution, so long as a precipitate continues to form This is collected on a filter, lightly washed and dried The greenish powder (ferrous oxalate) thus obtained is gently heated in a porcelain basin until it begins to glow and gradually change into a black powder which becomes a beautiful red when cooled.

The chemically pure ferric oxide thus obtained constitutes an excellent pigment for enamels, and is specially valuable on account of its fire-resisting properties It yields uncommonly well, so that a very small quantity is sufficent to impart a decided yellow colour to a large amount of enamel. It is to the presence of small quantities of ferric oxide, as an impurity in the raw materials, that the yellow shade exhibited by certain common qualities of enamel is due.

cooling. Special precautions—which will be referred to later—must also be taken in fusing the enamel masses coloured with this preparation.

By changing the proportions of ferrous sulphate and aluminium compounds in the mixture different shades of red can be produced. For instance, 10 parts of ferrous sulphate and 30 parts of alum, mixed and treated as above, will furnish a product imparting a handsome flesh tint to enamel.

The wealth of colour afforded by the ferric oxide preparations, combined with their cheapness, places them among the most valuable and most extensively employed pigments now used in the enamel industry

Gold Preparations

The preparations of gold serving for the production of purple red shades in enamels and glass masses yield the finest colours known, though at the same time the manufacture of the pigments (or rather their incorporation with the enamel mass) is the most difficult of all the tasks we have to deal with in this connection. Formerly, purple of Cassius was the sole means employed for the preparation of gold reds, but of late its place is frequently taken by pure gold chloride in combination with sodium chloride

Sodium-Gold Chloride.

This product—formerly also used in medicine under the name of gold salt, *Sal auri Figuieri*, or *Aurum muriaticum natronatum crystallisatum*—is prepared in the following manner: Gold, preferably in the form of gold ducats, which are made of very pure metal, is placed in a glass beaker standing in a basin of water, and covered with freshly prepared nitro-hydrochloric acid—*aqua regia*—composed of 1 part of nitric acid and 4 parts of hydrochloric acid, the reaction being assisted by the application of heat to the water bath.

When ducats have been employed no residue is left, the gold entirely dissolving, but if silver be present, an insoluble sediment of silver chloride remains behind The solution is poured off with care, and is evaporated to dryness in a porcelain basin at a gentle heat

Pure sodium chloride, in quantity equal to one-fourth the original weight of gold taken, is added to the dry residue and the whole is then dissolved in water and re-evaporated to complete dryness.

Tin-Gold Chloride

Nowadays the use of purple of Cassius for producing red on enamel is superseded by a compound chloride of tin and gold This is prepared in exactly the same manner as the double salt of gold and sodium just described, except that after the gold chloride solution has been evaporated to dryness it is re-dissolved in water and mixed with a solution of tin chloride A precipitate of tin-gold chloride is thrown down, which, after being collected on a filter and washed with pure water, is dried by gentle heat

Purple of Cassius

The substance known under this title is difficult to prepare, and its properties and colour differ according to the method of preparation adopted, a true gold purple of Cassius being formed only when a solution of gold chloride is brought into contact with a liquid containing both stannous chloride and stannic chloride.

Out of the numerous existing recipes for obtaining this preparation the following are known to be reliable —

Light Purple.

According to Wachter a light shade of gold purple can be obtained by the use of the solution of stannic chloride prepared by dissolving 5 grams of pure tin in boiling *aqua regia*, evaporating this solution to dryness on the water bath, and re-dissolving the mass in distilled water. On the other hand, a solution of stannous chloride is prepared by dissolving tin in hydrochloric acid, the metal being in excess. This solution is concentrated to a density of 1·7, and 2 grams are then added to the stannic chloride solution, the whole being diluted with 10 litres of water.

To this liquid is added a solution of gold chloride (prepared by dissolving 0·5 gram of gold in *aqua regia*, evaporating to dryness and re-dissolving in water), the whole being stirred thoroughly and treated finally with 50 grams of ammonia. The greater part of the liquid is decanted from the resulting precipitate, and the latter is then collected on a filter, washed quickly, mixed with 20 grams of lead flux whilst still moist, and finally dried.

This lead flux is compounded of a mixture of 2 parts of red lead, 1 part of quartz and 1 part of calcined borax.

The resulting preparation is amethyst in colour but may be converted into true purple by adding to it, when dry, 3 grams of dry silver carbonate—prepared by treating a solution of silver nitrate (*lapis infernalis*) with sodium carbonate, so long as a precipitate continues to form; then washing the latter and drying it.

Dark Purple

To prepare a dark purple, a solution of 0·5 gram of gold is diluted with 10 litres of water and mixed, by continuous stirring, with 7·5 grams of stannous chloride solution (sp. gr. 1·7) and a few drops of sulphuric acid The moist precipitate is mixed with 10 grams of lead flux and 0·5 gram of silver carbonate.

Rose Purple

Rose purple is obtained by dissolving 1 gram of gold in *aqua regia*, and mixing this solution with a solution of 70 grams of alum in 20 litres of water, and 1·5 grams of stannous chloride (sp. gr. 1·7), ammonia being then added so long as a precipitate continues to form. The precipitate is washed, mixed with 70 grams of lead flux and 2·7 grams of silver carbonate, and dried.

There are many other recipes for preparing gold purple, but in all of them the rule applies that, to obtain a good colour, the solutions employed must be very dilute. It should also be observed that the colour of the preparations themselves is no criterion of that imparted by them to enamel, an ugly brown-red purple, often producing the most beautiful shade, whilst a bright-looking preparation may yield shades the reverse of handsome.

The quantity of gold purple, or other gold preparations, required to produce intense coloration of the enamel, is very small, gold being characterised by a specially high pigmentary power.

Owing, however, to the trouble involved in its preparation and the irregularity of the results obtained, gold purple is going out of use as a pigment for glass, porcelain and enamels, and is being supplanted by tin-gold chloride, or by the double chloride of gold and sodium.

Cuprous Oxide.

A purple red, equal in beauty to that obtained from gold compounds, is produced in glass by cuprous oxide. Unfortunately, however, this substance cannot be used for enamels, owing to the readiness with which it is converted into cupric oxide during the repeated meltings necessary in the case of these preparations. As cupric oxide produces a bluish-green colour in glass the results are, therefore, liable to be erroneous.

ORANGE PIGMENTS.

No single preparation capable of producing an orange shade in enamel is known, but, as this colour is a mixture of red and yellow, it can be prepared by mixing red-forming and yellow-forming pigments together in suitable proportions. Success is, however, certain only when a preparation of antimony is used along with the red iron pigment (ferric aluminate), gold compounds are unsuitable, being too readily converted into metallic gold.

The resulting shade of orange obtained varies from orange yellow, when the antimony preparation preponderates, to a redder tinge when the conditions are reversed.

GREEN PIGMENTS.

Green enamel may be prepared in various ways by incorporating certain metallic oxides with the enamel mass, or by adding to the latter a mixture of pigments producing blue and yellow colours respectively. As, however, in this latter method the resulting shade of colour is less under control, besides being more troublesome, the direct process is generally adopted.

The oxides capable of colouring enamels green are ferrous oxide, cupric oxide and chromic oxide. Each of these develops its own particular shade of green, ferrous oxide yielding "bottle green" (the colour of common green glass), whilst copper and chromium furnish emerald shades of different kinds—readily distinguishable by comparing glasses tinted with these oxides.

Ferrous Oxide.

Owing to the inferior green developed by ferrous oxide, and the difficulties encountered in producing the colour, this substance is seldom used for colouring enamels. The author has, however, found that a very handsome shade is obtained provided the ferrous oxide be used in a perfectly pure state, the depreciation of the colour being occasioned by the presence of other metals, more especially manganese and copper, as well as by ferric oxide.

Ferrous oxide cannot be used as such, because when precipitated from combination it is converted, on exposure to air, into ferric oxide, which gives a brownish yellow. Consequently the only way to employ ferrous oxide is in the condition of a ferrous salt, taking care at the same time that the enamel mass is free from any easily reduced metallic oxide (*e.g.*, lead oxide). The mass can only be used as a transparent coating or "cover."

The best form of ferrous salt is pure ferrous sulphate, which can be most suitably prepared in the following manner: Iron is dissolved in dilute sulphuric acid, the metal being kept in excess, and the reactions assisted finally by gentle heat. The hot solution is filtered into a vessel containing an equal bulk of very strong alcohol, which is kept stirred during the operation in order to prevent the formation of large crystals. After leaving at rest, covered up, for twelve hours, the fine crystalline deposit of pure ferrous sulphate is dried quickly by pressing between layers of filter paper, and is then stored in properly closed vessels. It is added to the enamel, in a dehydrated condition.

This pure sulphate will yield an agreeable green, and one that is particularly suitable for use in imitations of old works in enamel.

Cupric Oxide.

Cupric oxide may be obtained by the direct method of heating fine filings of the metal to redness in a flat basin until they have become black, the metal having absorbed oxygen from the air and changed into cupric oxide. The complete conversion of the metal in this manner is nevertheless a lengthy operation; the product thus obtained, however, may be used to advantage as a green colouring matter for ordinary enamels. Special beauty of tone is furnished by a product obtained from chemically pure copper by the very simple method of preparation described below, which may be universally recommended.

To produce chemically pure copper, a number of pure zinc strips are placed in a large glass flask holding several litres, and over them is quickly poured a filtered solution of cupric sulphate (blue vitriol) up to about two-thirds the capacity of the flask, which is then closed and strongly agitated for some considerable time. On strongly heating the contents of the flask, a deposit of pure copper in the state of very fine powder is obtained, and the agitation of the vessel is continued until the liquid has become colourless. The latter is then filtered off and the copper washed with hot water, dried and calcined, whereby it is quickly converted into cupric oxide.

To ensure an extremely fine state of division the washed copper may be dissolved in nitric acid and re-precipitated as black oxide, by adding caustic potash to the boiling-hot solution.

The enamel colours yielded by cupric oxide may be toned by suitable additions of ferric oxide.

Chromic Oxide.

Chromic oxide green is often developed in enamels by the indirect method, wherein a certain proportion of potassium bichromate (acid, or red, chromate of potash) is added to the enamel mass, together with some deoxidising substance which reduces the chromic acid to chromic oxide, whilst the potash enters into combination with the vitreous enamel mass.

This method is used where no strictly defined shade of chrome green is required. Where, however, greater precision is exacted better results are obtainable from pure chromic oxide prepared in various ways, the handsomest colours being, however, obtained when the following method is pursued:—

Two parts of finely powdered potassium bichromate are mixed with 1 part of powdered sulphur, the mixture being then placed in a Hessian crucible—which it should only half fill—covered with a loose lid, and kept at a gentle red heat so long as the flame of the burning sulphur continues to appear. When cold, the contents of the crucible form a brittle, porous mass, which is finely pulverised in an iron mortar and then extracted repeatedly with water, containing a little hydrochloric acid to remove any iron present and which would spoil the colour. The residue of pure chromic oxide is finally dried by the application of heat

A very handsome but expensive chromic oxide, particularly well adapted for colouring enamels, is obtained by heating mercurous chromate, air being excluded. To this end mercury is dissolved in an excess of nitric acid, the solution mixed with potassium bichromate, and the precipitate dried and heated to redness in a porcelain crucible. The product is dried after repeated washings, and forms a very handsome green chromic oxide.

BLUE PIGMENTS

Cobalt is the sole blue-producing pigment at present employed in the enamel industry, no other being able to equal it in beauty of colour and productiveness. It may be used in various forms: as protoxide (chromous oxide), chloride, etc, as well as in the condition of a silicate, the so-called "smalt". Now the commercial varieties of smalt, though the finer amongst them are of handsome colour, are not good enough in this respect for use in the best enamels, and it is therefore desirable to obtain cobalt preparations that are free from impurities calculated to impair the colour. In this respect cobaltous silicate is superior to all other preparations, and should be made by every manufacturer of coloured enamels—the colour obtained surpassing all others in beauty. A reliable récipe for the production of this compound is given below.

Cobaltous Silicate.

This salt may be prepared from the cobalt ores: cobalt glance, smaltine, etc., by reducing them to a coarse powder and roasting them with unrestricted access of air, which volatilises—as white arsenic (arsenious acid)—the greater part of the arsenic usually present.

The residue, stirred up to a thick pap with concentrated sulphuric acid, is then heated to bright redness in a furnace and extracted with water The cobaltous sulphate resulting from the sulphuric acid treatment has the power of withstanding the action of very high temperatures, which decompose the salts proceeding from the other oxides in the air, and convert them for the most part into oxides or insoluble basic salts.

During the extraction of the calcined mass, only a small quantity of ferrous sulphate passes into solution along with the cobaltous sulphate. The former may be removed by the addition of small doses of sodium carbonate solution, which throws down ferric oxide as a brown precipitate, the end point of this reaction being easily detected after a little practice, since the cobaltous carbonate beginning to come down can be immediately recognised by its pale blue colour.

The cobalt solution thus freed from iron is filtered from the ferric hydrate precipitate, and is then treated with sodium silicate (water glass) to throw down cobaltous silicate. This pale blue precipitate is washed, dried and fused, in which state it forms a dark pure blue mass particularly well adapted for colouring enamels. A very small quantity of this silicate, when reduced to powder by quenching and grinding, is sufficient to impart a beautiful blue to the enamel mass.

Apparently the quality of the enamel mass exerts considerable influence on the intensity of the colour produced by this preparation and it is therefore necessary to ascertain from time to time, by fusion tests, the exact amount of cobaltous silicate required for the development of any given shade.

Cobaltous Zinc Phosphate

This preparation is used for producing very fine and pure-toned cobalt colours The simplest way to make this double salt of cobalt and zinc is by treating a solution of sodium phosphate with zinc sulphate solution followed by cobaltous sulphate the addition of the latter being continued until the colour of the precipitate has changed from its originally greenish tinge to dark blue.

This particularly handsome blue is generally applied in a flux composed of 2 parts of sand and lead oxide, and 42 parts of the double phosphate, to which 3 parts of pure cobaltous oxide have been added

By suitably varying the proportion of the cobalt compounds employed, all gradations of tone from pale blue to the very deepest shades can be produced

No matter what cobalt compounds are used, care must be taken that the cobaltous oxide is as far as possible free from certain oxides capable of impairing the purity of the colour Among these, ferrous oxide, nickelous oxide and manganese dioxide are the most injurious, the oxides of the other metals, although acting in a similar manner, being less powerful than these three.

An admixture of nickel, which is always present in cobalt ores, imparts a violet tinge so long as the enamel is hot, but the shade turns to brown in cooling and finally gives a reddish cast to the blue when cold.

A minute trace of ferrous oxide suffices to produce a greenish tinge, whilst a similar but less decided effect results from the presence of ferric oxide. Consequently, when iron cannot be totally eliminated, it should be converted into the ferric condition by means of oxidising agents, an addition of arsenious acid, saltpetre—or, in short, any substance capable of parting with oxygen at a red heat—being made to the enamel for this purpose.

Manganese dioxide imparts a violet shade to cobalt blue, whereas the protoxide has no injurious influence on the colour. If manganous oxide and ferrous oxide be both present they neutralise each other, so far as their effect on the colour is concerned.

Smalt.

Of all the cobalt compounds employed in colouring glass or enamel masses, none is so widespread as that manufactured in Saxony and sold under the name of smalt.

Chemically considered, smalt is a glass coloured an intense blue by means of cobalt, and most nearly resembling cobaltous silicate in composition and pigmentary qualities.

The manufacture of smalt need not be gone into in the present work, as enamel-makers will purchase their supplies and not attempt to prepare the article themselves. We will therefore merely give a general outline of the process.

The cobalt ore is roasted in such a manner that scarcely anything but cobaltous oxide is produced. The other metals are not oxidised but separate, mainly as arsenides, in the subsequent process of smelting, and constitute an important source of nickel.

The roasted ore is then fused with potash and silica, a cobaltous-oxide-potash glass being formed. This glass, on being poured into cold water, solidifies as a brittle mass, which is then stamped to fine powder and subjected to a very tedious process of washing by sedimentation, whereby the powder is separated into various degrees of fineness, a condition which exercises some influence on the intensity of colour. It is an essential condition, especially when fine enamels are in question, that none but the finest grades of smalt should be used; and by adhering to this rule an unimpeachable product can be obtained by the employment of this material in all cases where the attainment of the very highest degree of beauty of colour is not in question.

Cobaltous oxide is more productive than almost any other pigmentary oxide, and hence only a very small quantity of smalt is required to produce a very dark shade of blue. It is on account of this circumstance and the attendant relative cheapness of the pigment that cobaltous oxide is used for very common enamels, such, for example, as the dark blue kind now employed for enamelling the outside of cooking utensils.

Zaffre.

This substance, also erroneously termed "safflower," consists of finely powdered, roasted cobalt ore, and, being contaminated with all the other oxides usually accompanying cobaltous oxide, is therefore unsuitable for the production of really fine blues. Moreover, since the proportion of cobaltous oxide is by no means constant, fusion tests are invariably necessary to ascertain what the action of this preparation will be when added to enamel.

With reference to cobalt preparations, it should also be mentioned that they are not infrequently employed to counteract the slight yellowness produced in enamels by the presence of traces of ferric oxide, the blue furnished by cobalt being complementary to this yellow, so that the mixture of the two comes out perfectly white.

To correct the yellow shade due to iron, a small quantity—ascertained by two or three fusion tests—of some cobalt preparation is added, the result being the formation of a pure white enamel. If, however, the cobalt is in excess, the blue shade due to the latter will predominate, and the enamel will present a bluish-, *i.e.*, milk-white, appearance.

By the addition of pigments yielding green or yellow shades to preparations of cobalt every imaginable gradation between these colours and blue can be obtained. On account of its ability to withstand firing, and of its purity and colour, cobaltous oxide is one of the most valuable pigments available for the purposes of the enamel industry.

VIOLET PIGMENTS.

Only one single metallic oxide is known to be capable of producing violet; but this is one of such common occurrence in nature as to be available for the manufacture of cheap enamels. The substance in question is:—

Manganese Dioxide.

It is found native in many places, in the form of pyrolusite, and is won by mining, being in large demand for many industrial purposes (chlorine manufacture, cloth printing, dyeing, glass-making, the iron industry, etc.). The natural oxide (commercially termed "manganese") frequently contains a very high proportion of extraneous substances—ferric oxide in particular—and for this reason cannot be used in an unprepared state for the production of pure shades of colour. When this latter condition is essential, as it is in the case of enamels, chemically pure manganese dioxide must be used. To obtain this compound use may be made of the solution of manganese perchloride obtained as a by-product in the manufacture of chlorine gas, the liquor being boiled in a glass or porcelain vessel so long as chlorine gas continues to come off. This done, the solution contains only manganous chloride

A clear solution of calcium hypochlorite (bleaching powder) is then added until the deep brown precipitate of pure manganic hydrate ceases to form, which hydrate, when dried at a gentle heat, may be used direct as a pigment.

For ordinary purposes the finely powdered native oxide, which is a very powerful pigment, may be used, and, provided it be employed in merely small quantities, will produce very handsome shades of violet, the actual amount of iron present being then so minute that it cannot affect the colour.

Whichever material is taken, care is necessary, in fusing the enamel, to see that no reducing agents—such as particles of carbon, organic matter, etc.—are present either in the enamel mass or introduced therein from the fire, since otherwise the manganese dioxide, which readily parts with a portion of its oxygen, will be reduced to the non-pigmentary "red" oxide (Mn_3O_4, manganese proto-peroxide), and the enamel will become either colourless or assume a tone other than the one desired. It is by reason of this susceptibility to reduction that manganese dioxide owes its popularity as a decolorising agent in the manufacture of glass and enamels, a property which will be more fully discussed later on.

Being a very powerful pigment and extremely cheap, manganese dioxide is also used in preparing black glass and enamel, the addition of a somewhat larger proportion of the oxide than usual colouring the mass so strongly that it is only in very thin layers that the violet shade can be detected, thicker layers showing up quite black.

Brown Pigments.

In the true sense of the word, brown cannot be regarded as a colour, being usually a violet toned down by means of black; and, strictly speaking, there is no pigment known capable of imparting a brown shade to enamel, the nearest approach to a true brown being furnished by ferric oxide.

This shade is the well-known "bottle brown" already referred to, which may be regarded as a mixture of yellow, red and black, and is really a somewhat ugly gradation of orange.

A much better brown can be produced by mixing ferric oxide with a proportion of clay, or, as is done in some enamel works, making use of a clay ironstone. In the latter event, the production of a uniform shade of brown is evidently a matter of some difficulty—the only way to attain the end in view being to experiment with various mixtures until the desired result is produced.

When a preponderating quantity of ferric oxide is used, the fused enamels will exhibit a decidedly reddish tinge (puce); the addition of a yellow pigment will produce a yellowish brown, and so on.

BLACK PIGMENTS.

Although no direct black pigment for enamel is known, black enamels are easily prepared by employing some powerful metallic oxide, such as ferric oxide, cupric oxide, cobalt oxide, or manganese dioxide, in larger proportion than usual.

Each of the aforesaid oxides produces a characteristic colour, but when the amount taken is considerable the coloration becomes so intense as to appear black. Nevertheless a comparison between two such black shades produced by, say ferric oxide and manganese dioxide respectively, will show decided differences in tone However, to obtain an absolutely pure velvet black all that is necessary is to mix the said oxides together and fuse them with the enamel, the various individual shades being thereby neutralised and conjointly furnishing a pure black.

It is evident that in the case of enamel masses intended to be coloured in dark shades or black no particular care need be taken over the purification of the raw materials, the yellow tinge due to impurities being completely masked by the darker colour.

On the other hand, the contrary is the case when enamels are to be obtained pure white or in delicate shades; and in such event special artifices and adjuncts must be resorted to in order to attain a maximum degree of colourlessness in the mass, since it is only under these conditions that the full beauty of the superimposed colour can be brought out. Consequently, every enamel mass intended for artistic purposes must be subjected to a process of decoloration

VII.

DECOLORISING AGENTS.

The substances at the disposal of the enamel-maker for the purpose of decolorising the enamel mass are solely such as are capable of yielding up oxygen when exposed to high temperatures—usually red heat. The oxygen thus liberated within the body of the mass then exerts a powerful oxidising action on certain components, which would otherwise produce colour, and either converts them entirely into volatile products (carbon and organic matter being changed into carbon dioxide) or modifies them into a higher stage of oxidation whereby their pigmentary influence is diminished (*e.g.*, ferrous oxide to ferric oxide). The substances usually employed for this purpose are saltpetre, minium (red lead) and manganese dioxide.

Saltpetre (potassium nitrate) gives off oxygen at a low heat and is converted into potassium nitrite, which is decomposed by the silica in the enamel mass and forms potassium silicate, a substance then forming part of the matrix of the enamel. Sodium nitrate (Chili saltpetre) may be used in place of the potassium salt, but has an undesirable tendency to absorb water from the air, and therefore requires to be dried immediately before use.

Minium, as has already been mentioned, parts with oxygen at a red heat, and is reduced to lead oxide (litharge), which combines with the glass mass. Consequently, if plumbiferous enamel is to be prepared, minium may be selected with advantage as a decolorising agent. It must, however, be remarked that many colours cannot be developed in plumbiferous enamels; and hence when such colours are in question minium must not be employed

Manganese dioxide, as already seen, itself acts as a very powerful pigment towards glass and enamel, provided no reducing agents (carbon or ferrous oxide) are present, as these destroy its colouring power by degrading it to a lower stage of oxidation. Hence by adding to an enamel containing the above bodies a sufficient amount of manganese dioxide to convert them into carbon dioxide and ferric oxide respectively, the enamel can be decolorised, or its colour reduced to a faint yellowish tinge.

The greatest care is, however, necessary in the selection of the manganese dioxide for this purpose, since many of the commercial qualities contain as much as 30 and even 40 per cent of ferric oxide, and their use would result in the enamel being turned brownish-yellow instead of decolorised. It is essential therefore to take only the highest grades of commercial manganese dioxide, *i.e.*, such as are at least 90 to 95 per cent. pure, or better still the chemically pure oxide, since the amount required is so small that price is a matter of no importance.

No definite figures can be given as to the quantity of decolorising materials to be used, as this depends of course on how much of the substance (or substances) to be oxidised is present. The best, and, to the practical man, most convenient, means of ascertaining the amount required in each case is by fusion tests or trial smeltings, small samples of the enamel mass being fused and then compared with other samples of the same, fused with known quantities of a decolorising agent. In this way the object in view—the perfect decoloration of the enamel—will be rapidly and assuredly attained.

Fusion Tests.

For this and other laboratory purposes use is made of the small furnace shown in Fig. 2. This consists of an iron cylinder, *C*, lined with fireclay and serving to contain a large size Hessian crucible, *T*, in which is mounted on a wrought-iron tripod a small crucible, *S*, half full of magnesia, wherein is embedded the small porcelain or platinum crucible, *P*, serving for the reception of the material to be fused. The crucible, *P*, can be easily inserted and removed by means of a handle, *H*, of platinum wire. A conical cover, *A*, connected with a sheet-iron stovepipe, several yards long, serves to close the apparatus. Lump charcoal in pieces the size of a nut is placed in the crucible, *T*, through an aperture, *B*, which can be closed by a suitable cover. Twelve holes, *o*,

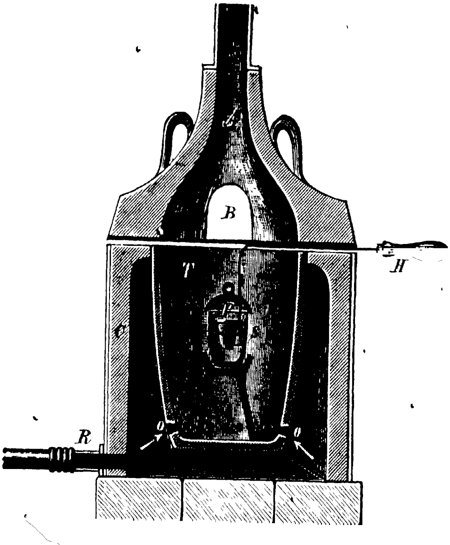

Fig. 2.

are bored through *T*, around the bottom. The pipe, *R*, supplies compressed air which before being discharged into the smelting fire is heated by passing through a coiled pipe in the same.

The temperature obtainable by the combustion of charcoal in the hot air blast is so high that the most refractory enamels can be fused in quantities of 100 grams (3½ oz.) and over, within a few minutes. Hence several tests can be performed within the hour and therefore a comparatively short time suffices to reveal the behaviour of a new mixture under fusion.

ROSSLER'S GAS FURNACE.

Wherever gas is laid on in the works, the enamel-maker can advantageously employ a gas furnace for making fusion tests. Such a furnace is represented in section in Fig. 3. The high, but narrow crucible, *A*, has a perforated bottom, the aperture being closed by a ball of porcelain. This crucible is mounted on a suitable fire-brick block and is covered by a thin bell-shaped fireclay vessel, *c*, which, in turn, is surrounded by a thick fireclay cylinder, *d* The lower part of the furnace is formed by an annular block of fire-brick, *b*, containing sundry small apertures on its inner side. Gas is supplied through a wide pipe *a*, to *b*, where it escapes through the aforesaid small apertures, and, mixing with air, is ignited The burning gas ascends round the crucible, *A*, makes its way out of the top of the bell-shaped vessel at *c*, and descends between the latter vessel and the outer cylinder to the flue, *e*, in which a strong draught is induced by means of a Bunsen burner, *f*.

As soon as the contents of the crucible, *A*, have melted, the porcelain ball floats on the surface and the molten mass falls down into a basin, *g*, filled with water. The lid, *d*, being removed, *A* can be re-charged, and in this manner several pounds of enamel can be fused in a very short time. Either of the furnaces just described can be warmly recommended for experimental purposes or for preparing very handsome coloured enamels for artistic work.

Saltpetre or minium affords the simplest means of decolorising enamel masses, because neither of these substances produces any colour if used in excess, whereas manganese dioxide stains the enamel violet. The following considerations must, however, be borne in mind, namely: an excess of saltpetre makes the enamel more refractory, owing to the formation of potassium silicate, whereas minium increases the fusibility of the mass, though diminishing its power of resisting chemicals and precluding the employment of certain pigments.

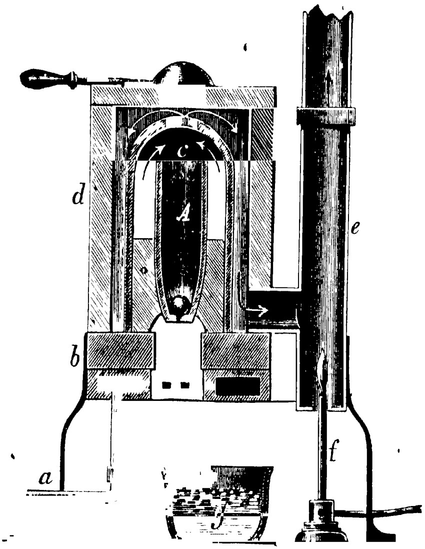

Fig. 3.

Since, however, the amount of saltpetre required to produce decoloration is usually so small that the refractory property of the resulting potassium silicate may be regarded as practically negligible, it is generally preferable to employ saltpetre for this purpose.

VIII

TESTING THE RAW MATERIALS AND ENAMEL MASS.

It is important that every maker of enamels should test not only the raw materials used but also the behaviour of the enamel mass when fused, this being the sole means whereby he is enabled to form an accurate opinion of the value of such materials and of the correctness of his formulæ

While a complete chemical analysis offers the surest means of obtaining the desired information, there are also simple methods available which enable the same to be gained, with a sufficient degree of accuracy for practical purposes, so far as the properties and mutual behaviour of the materials are concerned, and it is with these that we shall now proceed succinctly to deal.

The method always pursued is that of blowpipe analysis, the substances under examination being heated before the blowpipe flame, either by themselves or in admixture with other substances. The apparatus used for the performance of these tests is extremely simple, consisting of a spirit lamp, an ordinary metal-worker's blowpipe, a piece of platinum wire about four inches long, a strip of platinum foil of the same length, and a few sherds of white porcelain.

The blowpipe, in its most convenient form (Fig. 4) consists of a slightly taper tube inserted in a cylindrical piece from the side of which projects a second tapering tube, W, carrying a platinum cap or nozzle, P, which terminates in a narrow jet.

Before passing to the actual testing operations, a brief consideration will be given to the nature of the blowpipe flame, as many substances behave differently according as they are heated in the inner or outer portion of this flame.

The pointed blowpipe flame (Fig. 5) is produced by inserting the nozzle of the pipe in the flame of the spirit-lamp and blowing into it air inhaled through the nostrils and forcibly expelled into the pipe by contracting the muscles of the cheeks. On observing this conical flame it will be seen to consist of two well-defined conical zones, one inside the other. The inner cone, R, is highly luminous, whilst the outer flame, O, is inferior in brightness but is blue in colour. The former consists of gases which are capable of taking up oxygen, whereas the outer cone, in addition to completely oxidised bodies, contains free oxygen at a very high temperature.

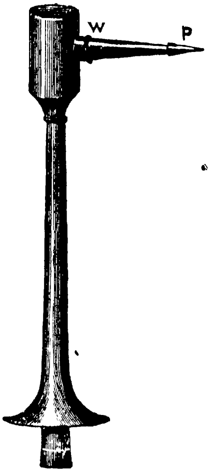

FIG. 4.

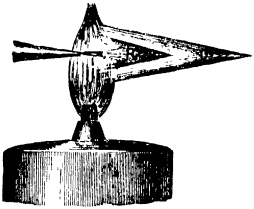

FIG. 5.

The behaviour of these two parts of the blowpipe flame towards various substances differs considerably, the properties of the two flames being entirely opposite, the inner flame, R, has the power of removing oxygen from bodies containing that element, and is therefore called the "reducing" flame; whilst the outer flame, by virtue of its content of glowing, free oxygen, exerts a powerful oxidising influence and is consequently termed the "oxidising" flame

For instance, if metallic lead be placed in a small hollow, on the surface of a block of charcoal, and exposed to the reducing flame it will simply melt and retain its metallic condition unchanged, but if the charcoal is now moved so as to allow the point of the oxidising flame to impinge on the molten metal the latter is rapidly converted into lead oxide, which on cooling remains as a fused yellow mass of litharge. On again moving the charcoal so as to bring the lead oxide under the influence of the reducing flame, the oxide will be deprived of its oxygen and again reduced to the metallic state

After prolonged exposure to the reducing flame a fusible substance (glass) containing iron will, when cooled down, exhibit a bottle-green coloration due to ferrous oxide, but if heated in the oxidising flame will acquire a yellow tinge (ferric oxide). These two results conjointly afford a sure proof of the presence of iron

TESTING RAW MATERIALS WITH THE BLOWPIPE FLAME.

The testing of the raw materials for the manufacture of enamel is usually confined to an examination for the presence of impurities calculated to affect the colour of the product. It depends on the nature of the substance to be tested whether it is examined by itself or with the assistance of reagents. Of course these reagents must themselves be pure in order to prevent false indications being given; and all such that fail to stand the test for purity must be discarded

Those raw materials that can be examined by the simplest means will be taken first In the case of these the method consists in moistening with distilled water the loop formed by bending one end of a piece of platinum wire, then dipping this loop into the substance to be tested, and fusing the adherent particles of powder in the blowpipe flame. These operations are repeated until enough substance is on the loop to fill it and form a bead, the colour of which can then be accurately judged by holding it before a white background (paper).

In testing for the commonest impurity (iron) in these materials, it is always advisable to employ the reducing flame, the green coloration produced by ferrous oxide being always more decided than the yellow tinge furnished by the same quantity of ferric oxide Moreover, when the presence of iron has been ascertained by the reducing-flame test, one is always able, from its subsequent behaviour in the oxidising flame, to ascertain whether the material is calculated to yield a colourless enamel if the mass be fused under conditions ensuring the complete oxidation of the iron.

Testing the Alkalies.

To test alkalies and the salts (potash, soda, common salt, Glauber salt, potassium sulphate) furnishing alkalies in the process of manufacturing enamel, the substance is first melted to a bead in the reducing flame, prolonged heating being necessary, especially for the carbonates. If the bead when cold has a green tinge, ferrous oxide is indicated; but, if perfectly colourless, no iron is present

Potash not infrequently contains manganese compounds, to detect which the potash is fused along with saltpetre to a bead, which is kept in a molten state for a short time at the tip of the *oxidising* flame. A green coloration in the cooled bead indicates manganese.

Practical experience will soon enable the observer to judge from the strength of the coloration whether the material under examination is fit for our purposes or not In the enamel mass manganese is converted into silicate, and as a rule the small quantity of manganese present in potash does not affect the properties of the enamel

The alkaline earths—lime, chalk, gypsum, dolomite, argillaceous limestone, barytes, witherite, etc.—are examined in the same manner, by heating in the reducing flame and noting the colour As, however, many of these substances are infusible before the blowpipe, recourse is had to anhydrous borax in order to obtain transparent samples

When carbonates are fused along with borax, the bead is at first turbid from the accompanying bubbles of carbon dioxide liberated by the boric acid, in such event the bead must be maintained in a state of fusion until all the gas has escaped and the mass becomes quite clear

The enamel fluxes—borax, boric acid, fluor spar and cullet—may all be tested for iron in the above manner, all that is usually necessary being to fuse them, without admixture, and examine their behaviour alternately in the reducing and oxidising flames.

Testing Silica

This substance, in the state of quartz meal and sand, is quite infusible by itself, and consequently has to be fused with an alkali, when tested for impurities, ordinary soda (of course free from iron, being generally employed on account of the fusibility of its bead. The mixture must be heated until all the carbon dioxide has been driven off, leaving the bead quite clear.

If the test fail to reveal iron in the silica or other substance under examination, but leaves the bead grey, yellow, or brownish after heating in the reduction flame, this coloration may be due to the presence of finely divided carbon.

This may be readily confirmed by reheating the bead with an addition of saltpetre—this time in the oxidising flame. In case the colour is the result of carbon or organic matter, these bodies will be consumed by the oxygen liberated from the saltpetre, and a perfectly colourless bead will be left on cooling.

Testing Lead Preparations

The object of testing preparations of lead—litharge, minium, white lead and lead sulphate—is twofold, namely, for the presence of copper or antimony as accidental impurities, and for adulterants, which not infrequently are intentionally added, especially to minium and white lead.

For the detection of adulterants it is generally sufficient to reduce the minium or white lead to the metallic state on charcoal before the blowpipe. If the resulting bead exhibits the ductility of lead, and no residue is left behind on the charcoal, the substance may be considered as pure. If, however, the bead is brittle, the white lead may have been adulterated with zinc white, the presence of which can be ascertained with certainty by reheating the bead in the oxidising flame. Under these conditions lead yields a yellow incrustation deposited on the charcoal in the immediate vicinity of the bead, whilst zinc oxide, which is more volatile, will be deposited a little farther away, and will besides show up yellow when hot, turning pure white on cooling.

A white infusible residue left behind on the reduction of white lead almost invariably consists of barytes, the powder in that case exhibiting a crystalline structure when examined under a magnifying glass. A red residue from the reduction of minium indicates ferric oxide, or, more frequently, brick dust. To distinguish between them, fuse with a borax bead in the reducing flame: a green coloration points to ferric oxide. A similar coloration is, it is true, furnished by brick dust, but in the latter case a much higher temperature is needed to fuse the mass than when pure ferric oxide is present.

To test lead preparations for the very grave impurities, copper and antimony, they must first be fused to a colourless bead with borax, then dipped in powdered saltpetre and heated in the oxidising flame a wine yellow tinge indicates antimony whilst copper gives a green bead which turns red after prolonged heating in the reducing flame, owing to the conversion of the cupric oxide into cuprous oxide If the bead is greenish yellow in colour, both copper and antimony may be simultaneously present to place the matter beyond doubt the substance must be subjected to the proper wet tests for these metals

Testing the Pigments

The object of examining the metallic oxides added to enamels is twofold—namely, to determine their purity and their behaviour in the enamel mass. The latter is a very important point in that it affords absolutely certain information as to the intensity of colour that may be looked for in a given enamel mass, and also as to the manner in which the fusing of the mass should be performed

In order to have a reliable standard of comparison for the colour reactions furnished by the different metallic oxides, it is desirable to prepare a series of borax beads tinged with oxides of known purity. By this means one is soon able to judge the colour reactions produced by the substances under examination, and acquire skill in detecting small quantities of oxides by the blowpipe test.

The method of testing the purity of metallic oxides is simple, and consists in fusing a minute quantity along with a borax bead or with a little of the enamel mass it is destined to colour. Since the quantity of oxide taken must be exceedingly small or the bead will be stained too deeply for the colour to be distinguishable by transmitted light, the bead of borax or enamel must first be fused until quite colourless, and, when cold, dipped in water and just brought in contact with the powdered pigment, sufficient of which will then adhere to suitably colour the bead

Should, after these precautions, the colour still be too intense, the bead is removed from the loop, and a fresh bead made and dipped in the powder furnished by the old one. By this means the colour is so diluted and lightened that an accurate judgment will become possible [*N.B.*—These tests must always be made by daylight]

The following colour reactions are furnished by the principal enamel pigments, with a borax or enamel bead, before the blowpipe —

	In the	
	Reducing flame	Oxidising flame
Iron	Bottle green	Reddish yellow
Iron and alumina	Bottle green	Red
Copper	Red	Emerald green
Cobalt	Blue	Blue.
Manganese	Colourless	Violet
Chromium	Emerald green	Yellow
Antimony	Yellow	Yellow
Uranium	Yellow green	Yellow green
Silver	Grey	Yellow
Zinc	Yellow when hot, colourless when cold	
Lead	Yellow when hot, yellow when cold	

It should be noted that, as already mentioned, strong (oxide) pigments such as ferric oxide, manganese dioxide, cobaltous oxide and cupric oxide, when used in somewhat larger amounts, produce deep black, in which event the colour must be diluted by fusing over again with a new colourless bead. Furthermore, that the colour of the beads while hot differs from that exhibited at the ordinary temperature; thus, beads containing lead or zinc are yellow when hot, whilst, on cooling, the zinc bead becomes colourless

TESTING THE ENAMEL MASS.

In order to examine somewhat larger quantities of enamel mass for colour a thin strip of platinum foil or, better still, a flat platinum capsule (crucible cover) about 1 inch in diameter may be used. This vessel being held by the tongs, the contents are fused before the reducing or oxidising flame of the blowpipe, until perfectly fluid. The fused mass can generally be separated from the platinum by careful pressure with a knife, especially when the cooling has been effected quickly.

In default of a platinum vessel a sherd of white porcelain will serve, but in this case the enamel generally fuses so tight on to the porcelain as to be rarely separable therefrom.

By means of fusion tests conducted in this way an idea is gained of the manner in which the enamel should be treated on the large scale. Thus if the reducing flame is found to injuriously affect the desired shade of colour, it will be necessary to take care in making the enamel to protect the mass from the reducing action of the furnace gases, or to add oxidising agents (saltpetre, manganese dioxide) to prevent any reduction.

The general description of the properties of the pigmentary materials and their behaviour in an oxidising or reducing atmosphere will also afford a guide as to the course to be pursued in fusing the enamel.

As the various enamels also react on the metallic surfaces which they are employed to cover, and modifications of colour may thereby ensue, it is also desirable to make fusion experiments in this direction. Such experiments may be easily performed by coating small strips of suitably prepared sheet metal (iron or copper) with enamel mass before the blowpipe, and examining the colour of the samples after cooling. This is a preliminary task which will afford important information as to the best thickness for the layers of ground and covering enamel—a point which will be reverted to in due course.

IX.

SUBSIDIARY MATERIALS.

As is the case in other chemico-technical trades, the manufacture of enamels entails the use of various subsidiary materials which, although not entering into the composition of the product, are yet essential for the preparation of the same However, in the branch with which we are now concerned, these subsidiary materials are few in number, and may be advantageously divided into four classes, *viz* : water, fuel, pickling materials and ammonium carbonate

Owing to the importance of these materials both in regard to the item of cost—in which respect fuel heads the list—and also to their influence on the resulting enamel, it is necessary to devote a few words to their consideration

WATER.

The principal use of water in the enamel industry is as a vehicle for the various materials during the operation of grinding; and the properties of the water employed may have a considerable influence on those of the enamel. Thus, if the water contains organic impurities in suspension, these will be retained, by the materials to be ground, just as in a filter, and as they will be carbonised in the subsequent process of fusion this may explain why, for example, some enamel-makers are unable to produce perfectly white or really handsome-coloured enamels in delicate shades

If the impurities present in the water are merely in suspension, the difficulty is easily got over by filtration through sand or, better still, an animal charcoal filter which will infallibly retain all solid bodies present.

A more injurious impurity in water for our purpose is sulphuretted hydrogen. This gas which is soluble in water, is a frequent product of the putrefaction of animal matter and the water from wells in the vicinity of cesspools or manure heaps is often largely contaminated by the gas.

Certain metals exhibit a very great affinity for sulphuretted hydrogen with which they form blackish compounds, two of the most susceptible in this respect being lead and copper. Consequently, when a lead preparation is ground in water containing sulphuretted hydrogen, the mass will turn to a decided grey, owing to the formation of the black compound, lead sulphide.

If the use of such contaminated water is unavoidable, it is advisable to add a small quantity of saltpetre to all plumbiferous enamel masses ground therein, so that in the fusing process the lead sulphide may be oxidised to sulphate.

The most delicate test for the presence of sulphuretted hydrogen in water is to boil the suspected sample in a vessel of glass or porcelain, and hold over it a strip of white paper saturated with sugar of lead (lead acetate) solution. A black coloration indicates the presence of sulphuretted hydrogen, the extent of the contamination being easily judged by the depth of the stain; if, however, the paper remains uncoloured, the water is free from the substance in question.

Almost every well water contains a small quantity of iron, generally unimportant so far as our purpose is concerned, but a large proportion of this metal is prejudicial. Its presence may be easily detected by acidifying a 2-litre sample of the water with a few drops of nitric acid, evaporating down to ¼ litre, and adding a few drops of potassium ferrocyanide solution. Well waters, almost without exception, will exhibit a blue coloration under this treatment; but if the tinge be merely a faint one the amount of iron is so small as to be practically negligible, so far as its influence on the colour of enamel is concerned. On the other hand, if a deep coloration is produced, or a blue precipitate is formed, the water must be regarded as highly ferruginous and likely to contain iron sufficient to spoil the beauty of delicate coloured enamels.

The presence of comparatively large quantities of iron can also be recognised by the formation of a flocculent brownish precipitation of ferric hydrate when the water is boiled. The lime and magnesia salts and sodium chloride, almost invariably present in well and spring water are unimportant for our purpose.

It is evident from the foregoing that the manufacturer of enamels should endeavour to obtain perfectly clear water, free from sulphuretted hydrogen or any appreciable quantities of iron compounds. When the water is intended for use in the preparation of certain pure pigmentary materials it is essential to employ nothing but distilled, or very pure well water.

FUEL.

In the enamel industry very large quantities of fuel are consumed, it being necessary to heat the masses to high temperatures in order to bring them into a state of fusion. In this connection not only is the cost of the fuel in relation to its calorific power a matter of some importance, but also the indirect influence the fuel may exert on the quality of the enamel mass should be considered. For example, when a fuel yields a large quantity of specifically light ash, it may happen that some of the latter gains access to the enamel mass and affects its colour. Wood ashes always contain small amounts of unconsumed carbon (hence their grey colour), and should a small quantity of this ash find its way into an enamel mass containing no oxidising materials, the upper layers of the mass would acquire a decided grey tinge. Still more injurious in this respect is the ash of certain lignites, which in addition to carbon, contains a considerable quantity of ferric oxide capable of colouring the enamel mass.

Where the draught in the enamel smelting furnace is defective, the products of combustion are likely to be highly charged with reducing gases, which will have an injurious effect on many coloured enamels, for instance, the emerald green shade produced by cupric oxide will, under such conditions, be invariably discoloured owing to the reduction of the cupric oxide to cuprous oxide.

Consequently, care must be taken to select a fuel that yields no flying ash, and to construct the furnace in such a manner as to ensure an efficient draught in order that the fuel may be completely consumed to carbon dioxide and water vapour.

The fuel at the disposal of the enamel maker includes wood, peat, lignite, coal, wood charcoal, coke, and, in some places, anthracite.

Under ordinary circumstances *wood* is too expensive for use as fuel in smelting enamels and is moreover attended with the inconvenience that it burns away very quickly, so that the fire requires frequent attention to keep it up.

Peat is of low calorific value, yields a large proportion of ash, and is difficult to use in furnaces on account of its bulky nature.

Wood charcoal, especially from hard woods such as beech, forms an excellent fuel in every respect, the ash being small, the combustion perfect, and the heating power considerable. Unfortunately in most places it is too expensive for our purpose, and it is only where wood is abundant that the use of charcoal is feasible. By reason of its high content of potassium carbonate, the ash from wood or charcoal can be utilised as a source of potash for the preparation of common enamels.

When *lignite* is used the dense, dark-coloured kinds should be chosen as these alone have a suitable calorific power, the light-coloured lignites, still exhibiting the structure of wood, being often in this respect barely superior to peat.

The best kinds of *coal* to use are the deep black, shiny varieties. Those containing pyrites cannot be recommended, as they give off, during combustion, large volumes of that highly reducing gas, sulphur dioxide Coals yielding a large quantity of soot are also unsuitable

Anthracite is an excellent fuel, consisting, as it does, almost entirely of pure carbon, its calorific value is exceedingly high, and it yields a smokeless flame However, to get anthracite to burn properly, the fire-box or hearth requires to be constantly charged with compressed air from a blower.

Coke, the well-known by-product obtained from gas-works, is somewhat similar to anthracite, in consisting mainly of carbon and little else beyond the ash constituents of the original coal. Owing to its porosity, however, it burns more freely than anthracite and can be used, without difficulty, in any furnace, etc., provided with a good draught. As, moreover, coke burns without smoke and furnishes only carbon dioxide and ash, the temperature developed being also very high, it forms an excellent fuel for smelting enamel, and can be obtained cheaply in all places where gas-works exist

GAS FUEL.

Gas forms the ideal fuel for the purposes of the enamel-maker. Ordinary lighting gas, when mixed with the necessary amount of air, gives a very hot, smokeless flame, but is too expensive to be thought of for our purpose The so-called generator system of heating, wherein the fuel is consumed at a central station, or generator, and the hot gases are led to their various destinations (smelting ovens, muffles, etc), through a series of pipes and valves, appears a very advantageous method.

In the author's opinion water gas offers the cheapest means of heating in enamel works, and he considers that this system should have the preference where reconstruction is decided upon.

PICKLING MATERIALS

The substances comprised under this term serve, in the enamel industry, to clean the metal surfaces to which the enamels are to be applied, i.e., to free the said surfaces from adherent oxides, since enamel will not stick on any but a surface of clean metal but will peel off be the film of oxide never so thin.

Out of the numerous acids capable of dissolving metallic oxides the one most generally employed is commercial sulphuric acid, which, however, is too strong to use as a pickle by itself and therefore has to be diluted, generally in the proportion of 20 to 22 parts by weight of water to 1 part of acid.

In mixing the two the acid must be poured into the water in a thin stream, with constant stirring, but on no account should the water be poured into the acid, since in that event the mixture heats so rapidly that portions are projected violently out of the vessel to the great danger of the operator. Sometimes the use of Nordhausen sulphuric acid (fuming acid) is advocated, but there is no advantage in this, as it is converted into ordinary acid on dilution.

Vinegar is also used as a pickle and acts by virtue of the acetic acid it contains, but is only advisable when it can be bought cheaper than sulphuric acid; the crude wood vinegar is the most suitable on account of its low price.

In some places a pickle is prepared from crushed barley or oats, stirred up with warm water and left to ferment. The product contains lactic acid, acetic acid and other organic acids, which constitute the active principle. It presents the disadvantage, however, of giving off a very disagreeable putrid odour after a short time; and, besides, the presence of the solid particles of meal increases the trouble of rinsing the metal when cleaned.

Consequently the cheap and strong commercial sulphuric acid forms the best pickle, and is more frequently used than any of the others mentioned.

AMMONIUM CARBONATE

This salt—often, though erroneously, called "ammonia"—is used in enamelling, to prevent the layer of enamel from cracking. At the present time it is obtained in large quantities as a by-product in gas-works, and forms colourless crystals which are coated over with a white powder and smell like ammonia.

Being extremely volatile, ammonium carbonate must be kept in tightly closed vessels, and preferably in a powdered condition. This method of storage is also best for all other fine materials, especially for pigments (which are often very expensive). Materials that are used in large quantities, such as purified quartz meal, powdered felspar, etc., may be kept in casks, dust being excluded by close-fitting lids.

PREPARING THE MATERIALS FOR ENAMEL MAKING

The purification and reduction of the principal materials have already been dealt with, and but little remains to be said on this matter. Hard substances such as quartz and felspar are difficult to pulverise in their ordinary state, but when quenched may be easily reduced in stamping mills, the resulting coarse powder being afterwards brought into an extremely fine state of division by grinding in suitable mills, and, if necessary, washed by sedimentation.

GLAZE MILLS

For reducing the hard materials, the so called glaze mills are used. These are of various patterns, but one chief point has to be borne in mind in their construction, namely that the substances to be ground must be kept out of contact with metal on account of the coloration produced by the particles of the latter worn away by attrition.

In small works use may be made of an ordinary grinding mill, in which the materials are ground in a wet state. The composition of the grinding rollers or millstones may be a source of inconvenience. A stone very rich in quartz, preferably a porous quartz rock, is generally used, but though of the seventh degree of hardness, such stones wear away very quickly, since the felspar to be ground is of the sixth degree, and the quartz also of the seventh degree of hardness, and on this account the stones of glaze mills require very frequent renewal—an expensive and tedious operation. Nevertheless it is not advisable to use millstones of any other material than quartz, such stones being usually much softer than the latter, and mostly containing ferruginous minerals detrimental to the quality of the enamel. It is therefore best, in large works, to proceed with the reduction of the materials in a systematic manner, somewhat as follows The material is calcined, then quenched, and broken down in a stamping mill, the resulting coarse powder being sifted and the fine siftings passed on for further treatment, whilst the remainder is returned to another department in the stamping mill

EDGE-RUNNER MILLS

The further treatment of the coarse powder is best performed by dry grinding in edge-runner mills These consist of a horizontal plate, in the centre of which revolves a vertical shaft, supporting a horizontal crosspiece which serves as the axis of a pair of circular millstones As the vertical shaft revolves, the millstones, rotating on their axes, describe a circle on the horizontal bottom-plate, and pulverise the material lying thereon, scrapers being employed to bring the material continually into the path of the rollers Figs. 6 and 7 show the arrangement of a recognised excellent edge-runner mill fitted with a revolving bottom-plate, G, which takes the form of an annular trough, actuated by a bevel wheel mounted on the vertical shaft, J, and receiving motion from the driving pulley, N, through the cogwheel, O, on the horizontal shaft, C The shaft, J, is attached at the bottom to the trough, and runs on bearings, M and L The rollers or runners, H, revolve on a fixed horizontal shaft, their movement resulting solely from the friction produced by the material under treatment between the runners and the bottom of the trough. The material is kept in the path of the rollers by means of scrapers provided on the bottom-plate.

The material delivered, in the state of coarse sand, from the stamping mill is ground by the edge-runners to the fineness of ordinary sea sand and is then transferred to the ordinary mills. If a still finer and more homogeneous product

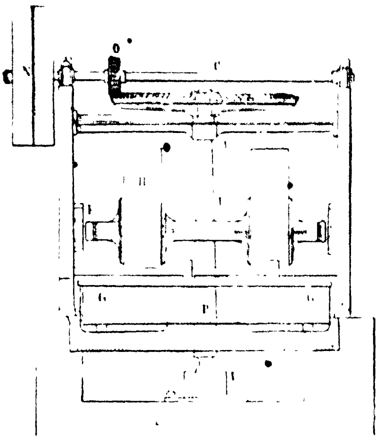

FIG. 6.

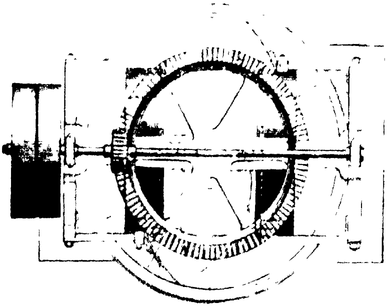

FIG. 7.

is required, which is seldom the case unless for special qualities of enamel, the powder coming from the mills is washed by sedimentation, the coarser particles being used for ordinary enamels and the finer for those of higher quality.

When washed in this manner, or ground in a wet state, the drying of the materials entails great care. With this object the pulpy mass is spread out about two inches thick on cloths stretched upon frames, the layer being covered over by other cloths and left to dry at the ordinary temperature in summer, whereas in winter time the waste hot gases from the smelting and calcining ovens are utilised for heating the drying rooms containing the aforesaid frames mounted on racks.

In an enamel works of any size several sets of mills must be provided, together with a reserve of millstones ready for use, as the stones wear away very quickly and frequently need trimming, and it saves time to change them before they get worn down and untrue.

Tin oxide being already in a very finely divided state needs no grinding, but only requires levigating to remove the particles of metal present.

Comparatively soft materials such as lime, soda, etc., are reduced either in a stamping mill or by pounding in a mortar, and passed through a fine sieve, so that all the materials required for preparing the enamel mass are in as finely divided a condition as possible, ready for use and fit for mixing.

The foregoing treatment of the raw materials though expensive is a necessary and absolutely indispensable process, as it is only when the greatest care has been bestowed on the preparation of the materials, and they have been reduced to the finest possible condition, that one can count on obtaining a readily fusible and perfectly homogeneous enamel.

XI

MIXING THE MATERIALS

From the theoretical explanation of the changes taking place during the formation of glass it follows that, in the fusing of the enamel mass the individual materials (silica, lime, soda, etc.) must be in an extremely fine state of division and intimacy of admixture. If the operation of mixing is not properly carried out, the enamel obtained by fusing the various materials together will not fulfil expectation but may exhibit considerable irregularities in points of composition and fusibility. Thus, for example, if one part of the mass contains a large proportion of quartz and lime with a relatively small amount of soda, this portion will form a very refractory enamel, whilst in the remainder the converse conditions prevailing will render the product extremely fusible. That an enamel of such irregular character will give rise to difficulties in the course of its application to a metal surface requires no demonstration.

Consequently, uniformity of admixture throughout the entire mass is an indispensable feature, and one entailing great care in the mixing process.

MIXING BARRELS

The most serviceable method of mixing the raw materials for enamel is that wherein use is made of very strong barrels, with wide bungholes provided with tight-fitting covers. A shaft is passed through the ends of the barrel so that the latter can be rotated upon the axis thus provided. The barrel being charged about two-thirds full with weighed quantities of materials according to the recipe for the enamel to be produced, is caused to rotate slowly on its axis, whereby the materials are thrown together and incorporated with one another.

The time required to produce a thorough admixture of the contents of the barrel can only be determined by experience, and chiefly depends on the size of the vessel the operation being more quickly completed in small barrels than in those of large size

Since the fused enamel mass has to be ground up again, it is evident that a considerable amount of motive power is required in a large enamel works The cheapest form is water power, when sufficient is available for driving the edge-runners, grinding mills and mixers. In default of water, steam is the least expensive, the engine being preferably mounted in a central position for driving the machinery, so as to reduce the cost of mounting, and loss of power in driving long shafting

To economise fuel it is advisable to utilise the heat of the waste gases from the furnaces to dry the raw materials, and, where possible, to assist in heating the boilers, warming the water needed for other purposes in the works, etc., in a word, to utilise the fuel to the utmost.

THE PREPARATION OF TECHNICAL ENAMELS

XII

THE ENAMEL MASS

IN the preceding pages, enamel masses have only been dealt with generally, the method of preparing the raw materials being the same in all cases. Although many makers carry out the process of enamelling in one operation and with a single enamel mass, it is nevertheless preferable to divide it into two stages and employ two separate enamel masses. This is particularly important when it is desired to produce enamelled goods able to withstand repeated exposure to high temperatures, as is the case with cooking utensils.

Only when the composition of the enamel is such as to enable the latter to expand and contract in sympathy with the metal to which it is applied will the coating remain intact after the article has been a long time in use. If, on the other hand, the enamel is unable to follow the fluctuations of the metal, the inevitable consequence will be that in a short time innumerable small fissures—invisible at first—will be produced, and the enamel—losing its hold on the metal—will begin to chip off.

At the time when the manufacture of enamelled goods, especially cooking utensils, began to be carried on on a large scale, sufficient attention had not been bestowed on this circumstance, and consequently most of the enamelled ware produced suffered from the defect that the glaze was soon rendered unsightly by the aforesaid cracks, and quickly began to chip off—a behaviour which greatly retarded the general extension of enamelled goods for domestic purposes, by reason of the lack of durability exhibited by this somewhat expensive ware

For a long time endeavours have been made to produce enamel masses possessed of sufficient properties of expansion and not liable to crack and chip off, but this object was not attained until the practice was adopted of replacing a single layer of enamel by two, of different molecular and chemical properties, the one mass being termed the ground, and the other the covering layer.

THE GROUND LAYER

As its name implies, the ground layer of enamel is the one applied direct to the surface of the metal, and separating the latter from the covering layer With regard to the properties of the ground layer it should be noted that the mass should be of a very refractory character, and only sintered, without being actually fused, upon the surface of the metal, so that it covers the latter, not as a perfectly coherent coating but as a porous mass It is as a result of this porosity that the metal is able to expand and contract rapidly without causing a separation of the constituent particles of the ground layer of enamel.

THE COVERING LAYER

This layer which acts as a glaze towards the ground layer, is invariably compounded in such a manner as to be more readily fusible than the latter, and to unite therewith at the surface of contact, so that the enamel exhibits, in the finished state, a gradual transition from the covering layer, through an intermediate mixed stratum, to the ground layer.

The method of treating the masses intended to form the covering and ground layers of enamel varies according to the amount of care exercised in different factories. The most effective method, and the one best calculated to produce good results, is undoubtedly that wherein the mass resulting from the fusion of the materials is re-ground, then applied to the object to be enamelled and fused thereon, the operation being the same in the case of the cover enamel.

The repeated fusings make this process expensive, and therefore many attempts have been made to cheapen it by modifications, none of which, however, have succeeded in yielding equally good results.

In the case of cheaper ware, the preliminary fusing of the ground layer enamel is omitted, the mixed raw materials being applied direct to the surface of the metal and melted thereon. The cover enamel is then usually dusted on in the form of powder, and fused. Provided sufficient care be exercised, perfectly unimpeachable results can be obtained by this method, though in no case is the ware so durable as that prepared by the aid of previously fused ground and cover enamels.

As, notwithstanding their lower price, the less carefully prepared goods cannot compete with those manufactured with greater attention to suitable precautionary regulations, it is to the interest of every maker of enamelled ware to use none but previously fused enamel masses, and to discontinue the practice of melting the enamel mixture direct on the metal.

XIII

APPLIANCES FOR SMELTING THE ENAMEL MASS

Formerly the smelting of the mass was performed on small quantities at a time, owing to the difficulty then standing in the way of working with larger amounts, especially in the case of very refractory enamels The chief cause of the reluctance of makers to carry out this important operation was on account of the enormous quantity of fuel consumed in the furnaces, but since the great progress made in the construction of the latter, the difficulty has been abolished, the heat employed being now fully utilised

CRUCIBLES

The smelting of glass masses is generally effected in large pots or crucibles of special shape and method of arrangement in the furnace, and a few words will be devoted to these crucibles before passing to the description of the furnaces.

It is naturally indispensable that the crucibles should be made of perfectly fireproof materials, since they have to withstand strong white heat; and as they are rather expensive it becomes necessary to make them serve as many times as possible.

In most works the so-called Hessian crucibles are used for smelting the enamel mass, these appliances being excellent for this purpose in so far as their high fire-resisting properties are concerned, the highest temperature of the furnace producing no further effect on them than a slight sintering of the edges. Nevertheless, the chemical influence exerted by the materials of the Hessian crucible on the enamel mass is a very important consideration. Masses rich in basic substances, *e.g.*, soda, attack these crucibles to a considerable extent and form, at the surface of contact, highly refractory compounds. Furthermore, the iron compounds present in the crucible material make their way to some extent into the enamel and produce coloration, these results ensuing more particularly while the crucibles are still new, since the highly refractory layer, formed by combination with silica on the walls of the crucible during the smelting of the first charge, constitutes a kind of glaze which, in subsequent use, both preserves the crucible from further corrosion and prevents the contents from becoming contaminated.

The chief cause operating to spoil the crucibles is, usually, the practice of refilling them with a fresh charge whilst still in the furnace immediately after the fused charge has been run off through the aperture provided for the purpose at the bottom of the crucible. At the moment of emptying, the crucible is at the maximum temperature attainable in the furnace, and if now the fresh charge of comparatively cold materials be introduced at once, the result is that cracks are liable to be produced, which constantly increase and often terminate in the breakage of the crucible just at the moment when it is full of fused material, thus causing a great waste of time and stuff.

It not infrequently happens that a crucible is already spoiled before it has been used at all, since when left exposed to the air for some time the crucibles have a tendency to absorb moisture, in a quantity sufficient—though in itself small—to cause them to crack if exposed to the heat of the furnace without due precaution. Thus when put suddenly into the hot furnace, the water contained in the pores is converted immediately into steam, which by its rapid efforts to escape gives rise to cracks in the mass of the crucible.

Consequently, in all large enamel works, where the furnaces are in constant use, it becomes important to prevent as far as possible the damage and inconvenience arising from the breakage of the crucibles in this manner. To this end, each crucible is very carefully examined, rejecting any that appear defective, and placing the sound ones to dry, a very suitable method of carrying this into effect being to keep a number of the crucibles on the dome of the furnace, though a special drying chamber, heated by the waste gases from the furnace, is still better. The crucibles being thereby thoroughly dried can then be set in the furnace without any fear of cracking.

It is highly advisable to warm the charge of material to be smelted in a separate chamber before filling the crucibles, since this procedure not only helps to prevent the cracking of the crucibles, but also to reduce the time occupied in fusing the mass, the work being greatly simplified when this preliminary heating is effected in a vessel from which the charge of warmed-up materials can be run direct into the crucibles. The most suitable vessels for this purpose are made of fireproof materials, and shaped like a flat, oval basin with four strong lugs at the side, by means of which the vessel can be lifted with a corresponding iron fork.

When a crucible is to be charged, one workman lifts the warming-up pan out of the chamber by the aid of the said iron fork, and slides it over the edge of the crucible, a second workman thereupon tipping up the pan, by means of a hook acting on a projection at the back, so that the contents are discharged into the crucible. A vessel and fork of the kind just described are shown in Figs. 8 and 9 respectively.

In some works it is the custom to use the salts (*e.g.*, borax, soda, etc.) employed in the enamel mass, direct without previously depriving them of contained water, a practice that should, however, be deprecated on account of the difficulties to which it gives rise in retarding the fusion of the mass, etc.

The proper course to pursue is to work with dehydrated materials which have been stored in tightly closed vessels and mixed with the other ingredients in the revolving barrels

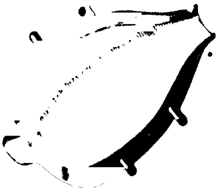

FIG. 8

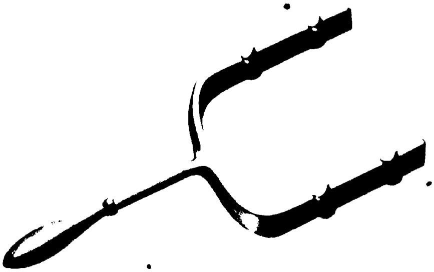

FIG. 9

already mentioned, the mixture being promptly placed in the warming-up chamber to prevent any absorption of moisture.

Unglazed porcelain crucibles are highly recommendable though somewhat expensive. Ordinary porcelain, however, is not suitable for this purpose, its composition being such that it sinters when exposed to the heat of the smelting furnace. This behaviour is due to the presence of such a large proportion of felspar, which fuses under the great heat employed, and forms a matrix surrounding the quartz and kaolin.

Consequently the porcelain crucibles for smelting enamels must be prepared from a mass endowed with very highly refractory properties and perfectly fireproof—an end easy to attain by reducing the content of felspar to a minimum, and correspondingly increasing the proportion of kaolin.

Such a crucible, if properly treated at the first time of using, becomes excellently adapted for the fusion of enamel masses. When the first charge is smelted, the interior of the crucible becomes coated with a thin layer of glaze—more refractory than the rest of the contents and remaining unaffected by subsequent charges. Porcelain body being always made from pure, *i.e.*, iron-free) materials there is no danger of the enamel mass being contaminated with iron, even the first time of using the crucible.

Experience teaches that the crucibles last longest when kept constantly hot and prevented from becoming cooled through the admission of cold air or charging with unheated materials. For this reason the furnaces should be in work continuously, the crucibles not being removed or allowed to cool until they are worn out or the furnace is to be shut down for some time. In the latter event the dampers are closed, so that the fire burns out slowly and the furnace afterwards gradually cools down, the crucibles not being removed until cool enough to handle; they are then carefully examined, especially near the bottom, before being used again.

THE SMELTING FURNACE

The furnaces formerly in general use for smelting enamel masses were of the vertical type shown in section in Fig. 10. In the centre of the hearth is a circular opening containing a cylinder of fireproof material extending downwards through the ashpit into a chamber underneath whilst the upper end projects a short distance into the furnace and, being cut off flat at the top serves as a support for the crucible. The furnace is supplied with fuel through the top, and the chamber below the ashpit contains a tub of water to receive the molten mass of enamel.

The crucible is fitted with a lid, which projects beyond the walls all round and is provided at the top with a knob

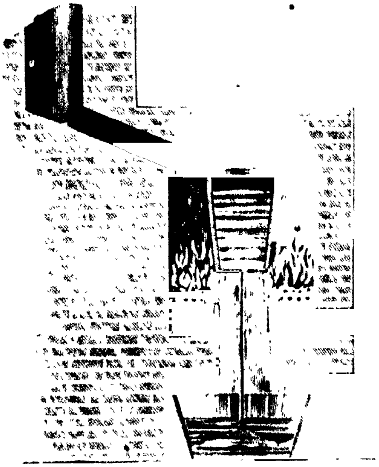

Fig. 10

for lifting. The bottom is perforated with an aperture which is closed, each time the crucible is re-charged by means of a layer of quartz meal mixed to a paste with water.

A number of such furnaces (e.g. six) may be arranged round a central flue to carry off the products of combustion, and, by a slightly modified construction, the waste gases can be diverted, first into the heating-up chamber and then under the pan for calcining tin or into the room for drying the ware to be enamelled, etc. In such case it is advisable to make the furnace of such a shape that the fuel is admitted, not through the top, but by an aperture in the side, a little higher than the upper edge of the crucible, so that the contents of the latter can be examined, the plug at the bottom knocked out, and a fresh charge inserted.

The arrangement of this class of furnace exhibits great similarity with that of an ordinary glass furnace, and is more economical in consumption of fuel than when each crucible has to be heated separately.

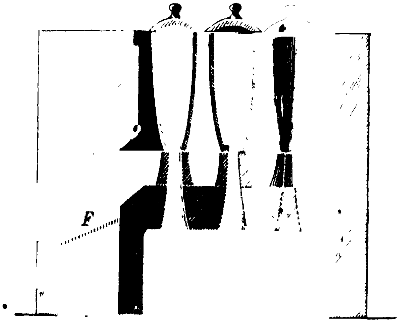

FIG. 11

For larger establishments, the author has designed a furnace to hold nine or twelve crucibles, as shown in section in Fig 11, and in plan in Fig 12. The crucibles are mounted on conical supports, resting on an arch under which the vessels for catching the molten mass are situated. The heat for melting the charge in the crucibles ascends from two hearths, F, and the object of the partition walls, S, is to unite the two currents of hot gases and convey them to the chimney, E. The top of the furnace is formed of a thick fireclay plate pierced with nine (or twelve) openings into which the crucibles fit, the latter being very tall in proportion to their breadth, in order to hold a larger quantity of the enamel mass, which shrinks considerably in bulk as it fuses.

For works of extra size the best smelting furnaces are those wherein the crucibles, instead of being exposed directly to the burning fuel, are heated by generator-gas produced in a separate furnace. In this case the crucibles are arranged to stand quite free, and may be enclosed in separate cells to which the admission of hot gas is regulated by dampers.

The most advantageous position for the generator is a central one with regard to the crucibles, which are arranged in a circle, and this furnace may be heated with the cheapest fuel, such as slack coal or lignite, the gases yielded by which are of high calorific power, so that the fusion of very refractory enamels is effected with ease.

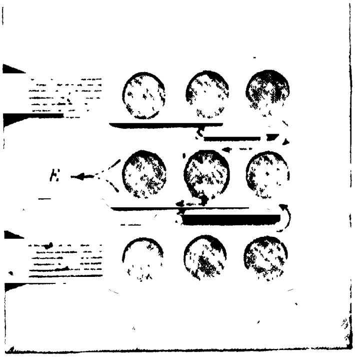

Fig. 17.

ELECTRIC SMELTING.

Nowadays the electric furnace furnishes much higher temperatures than are attainable in any other kind, and it is therefore a point worth considering whether the heat of the electric arc cannot be utilised for the smelting of enamel masses and other refractory glasses. This is undoubtedly within the bounds of possibility, all that is necessary being to bring the material under treatment under the influence of the arc, in a suitable manner, for the mass to fuse instantaneously, whereupon it may be caught in a crucible The latter should of course be kept hot enough in a suitable furnace to maintain the fused mass in a liquid condition. When full, the smelting is interrupted while the crucible is being emptied and replaced, whereupon the circuit is again completed and the operation resumed. The most refractory potash-lime glasses can be fused in this manner with ease; but whether the same process is suitable for lead glass requires to be determined experimentally, since in view of the powerful reducing action of the electric arc it is possible that the lead oxide may be reduced even in presence of silica the result being to modify the character of the glass produced

XIV

SMELTING THE CHARGE

In this operation all the precautions imaginable must be taken to prevent loss through the breakage of the crucibles, especially the first time they are used. The following is the method pursued :—

The crucibles, after being carefully examined, are bored with a conical steel bit, of sufficient breadth across the bottom to make an aperture large enough to allow the fused mass to run out. As the ground enamels are never so fluid as those intended for the covering layer, the holes in crucibles for fusing the former must be larger than the others, i.e., about ¾ inch in diameter, as compared with $\frac{5}{16}$ to ½ inch.

The object of making the holes taper is to facilitate the removal of the plugs, with which they are closed while the mass is being fused. These plugs are preferably made of quartz meal, moistened with gum water so as to form a plastic, coherent mass which, under the heat of the furnace, sinters together and prevents the contents of the crucible from escaping until the plug has been displaced by the insertion of a pointed iron rod. When the crucible is to be charged anew a fresh plug must be made and put in, and with this object the necessary quantity of plastic material is fixed on the tip of an iron rod, by means of which it can be pressed into the plug hole, an iron disc faced with clay being provided on the rod to protect the operator's hand from the heat of the furnace.

Unfortunately it often happens, particularly when the plug is made rather too large, that the crucible cracks on coming into contact with the cold damp mass. To avoid this evil the author generally uses well-fitting plugs of wrought iron attached to wrought-iron rods, the lid of the crucible being then provided with a slit extending nearly to the centre —or, better still, divided in two pieces through the middle— to admit of the insertion of the rod. Fig. 13 shows the arrangement of a crucible fitted with such an iron plug.

To prevent any injurious results accruing from the presence

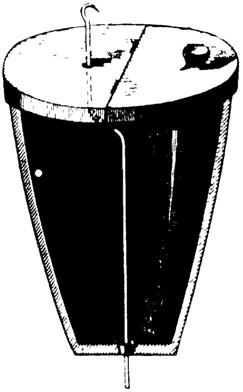

FIG. 13.

of iron in contact with the enamel mass, this rod and plug are previously coated with an enamel of such refractory character that, though fusible at a very high temperature, it remains solid at the temperatures attained in smelting ordinary charges.

If, when the plug is raised to allow the molten enamel to run out, it is lowered again before the crucible is quite empty, the aperture will be effectually sealed by the solidification of the residue on the introduction of the comparatively cool fresh charge of materials. Subsequently, when the contents again reach a state of fusion, the plug is kept down in position by the weight of the charge.

Another plan for keeping the plug rod upright is to bend it sideways and then upwards, passing the upper end through a hole in that half of the lid which is kept permanently on the crucible, the other half of the lid being taken off when the charge is to be renewed (see Fig. 13).

The crucible being filled almost up to the brim with the charge of anhydrous materials, the lid is put on and the crucible set in the furnace, whereupon the latter is heated up gradually, by first throwing in a two-inch layer of glowing fuel on to the hearth, and then adding cold fuel until the crucible is entirely surrounded therewith.

When the whole mass of fuel is in a glowing condition, more is added from time to time and the contents of the crucible are examined at intervals. However tightly the charge may have been packed at first, it settles down considerably in fusing, and then further quantities are added by degrees, until at last the crucible is full nearly to the brim with the molten enamel mass.

To ascertain whether the contents are all liquefied, a hot iron rod coated with very refractory enamel is inserted in the crucible, when, if it is found that the rod can be moved about freely without meeting with any appreciable resistance, it may be considered that the mass is properly smelted.

With a little practice the operator will be able to judge, by time alone and without the aid of the test rod, whether the contents are fused; nevertheless it is always advisable to use the rod before letting the charge run out, as it may happen, despite the care taken to ensure proper admixture of the materials, that some parts of the mass are more refractory than the rest, in which event the rod is the only reliable test.

Before allowing the charge to escape, the furnace is fired briskly for about ten minutes, in order that the great heat may render the mass extremely fluid, free from air bubbles, and able to run away with ease.

Special precautions must be taken throughout the entire operation to protect the contents of the crucible from the action of the furnace gases, and prevent access of particles of fuel. In the case of ground enamels of common quality, less vigilance is required than when fine covering enamels are being fused, or when coloured masses containing easily reducible metallic oxides are in question.

Thus, if, for example, a mass coloured green by cupric oxide were fused in an open crucible or one allowing particles of carbon to gain access to the contents, the inevitable result of this neglect of the requisite precautions would be the production of an enamel discoloured, or even red, in the upper layers, from the reduction of the cupric oxide to the cuprous condition. Consequently the crucible lids should be made to fit very close and must not be kept open any longer than is absolutely necessary, furthermore, an addition of some oxidising agent—saltpetre or manganese dioxide (the latter in very small amount)—should, unless injurious in other respects, be made, in order to counteract the reducing influence of the furnace gases.

Despite all precautions, it occasionally happens that some parts of the fused and re-solidified mass exhibit a brown or black streaky appearance, in which case these coloured portions should be picked out from the remainder, in order to prevent the whole being spoiled during re-melting. The discoloured pieces are set aside, and, when enough has been collected to fill a crucible, are fused over again with an addition of 5 per cent. of saltpetre. If the discoloration has been produced by carbon, the latter will be completely consumed by the oxygen liberated from the saltpetre, whilst if the result of ferrous oxide, the latter will be converted into the less powerful pigment, ferric oxide.

This latter oxide being moreover, disseminated throughout the entire mass has only a very slight effect on the colour, and therefore does not spoil the enamel for use as a ground layer. It must nevertheless be borne in mind that the addition of saltpetre will result in a modification of the fusibility of the enamel, to correct which a corresponding amount of silica should be added before the mass is remelted. By this artifice the original properties of the mass can be restored.

In most works it is customary to fuse the mass for ground enamel only once, and let it run off into the water tubs underneath some makers waiting until the molten mass has so far loosened the silica plug at the bottom that the fluid begins to trickle through. It is needless to say that this practice cannot be commended as in many cases it leads to a great waste of time and heat merely for the purpose of loosening the plug, and therefore crucibles should be preferably fitted with the iron plugs already described.

When fine cover enamels are in preparation it is scarcely possible to finish them properly by a single smelting, since they generally appear full of small bubbles when only once fused, and consequently require melting a second (sometimes even a third) time. However by increasing the heat as much as possible after the mass has become liquid in the second fusing, it will generally be found that this treatment suffices to furnish a product free from bubbles, the mass being thereby rendered thin enough to allow the bubbles to ascend and dissipate.

Quenching the fused mass in cold water makes it brittle and easily reduced to powder by stamping and grinding. The usual course is to allow the quenched material to accumulate for a certain time, then dry carefully, weigh, and send to the stamping mill, after which it is ground and weighed again, the frequent weighings being for the purpose of estimating the percentage of unpreventible waste, which occurs during the handling of the material and differs according to the nature of same.

Grinding is invariably effected with the assistance of pure water, the usual quantity employed being three times the weight of the dry matter treated. The operation necessitates the greatest care, and the product must be as fine as flour, since each coarse granule will cause a defective spot when the mass is used for enamelling.

Even in the case of technical enamels great care must be taken in the grinding, since granular fragments will cause the enamel to blister when put on the ware, and leave a bare surface of metal exposed to the injurious action of corrosive liquids, and although these defective places can be made good, the operation is troublesome, and prevention, by properly grinding the enamel, is better than cure

XX

COMPOSITION OF ENAMEL MASSES

It has already been stated in previous sections that enamels are nothing more than glasses coloured or rendered opaque by means of certain added substances.

As enamels are used for highly divergent purposes it becomes very important to modify their composition in such a manner as to best fit them for the particular object for which they are destined. Enamels intended solely for artistic embellishment must, above everything, exhibit beauty of colour and high lustre, resistance to chemical influences being in this case a minor consideration; whereas the main point in technical enamels is a suitable composition to enable them to effectually withstand chemicals and changes of temperature.

Consequently the composition of enamel masses has to be regarded from very different points of view, according as the products are intended for technical or artistic purposes, and the first question to consider is by what means the fusibility of the mass can be modified so as to be rendered more refractory or more fusible according to the requirements of the case.

It may be laid down as an axiom in this connection that: the higher the proportion of silica in relation to the other constituents, the more refractory will the product be and therefore the greater its hardness and powers of resistance against chemical agencies. Consequently, if it were possible to fuse silica by itself, a glaze of pure silica would form an ideal enamel for technical purposes. This being, however, impossible, the silica has to be mixed with basic substances in order to obtain a fusible mass.

The most refractory and durable enamels are furnished by masses consisting entirely of potash and lime, in addition to silica, since such masses are really nothing more or less than very refractory glass. As it is the object of every enamel-maker to produce a constantly uniform article, manufacturers are strongly recommended, in their own interest, to compound small quantities of these materials in various proportions, and thus ascertain by trial smeltings how these mixtures behave and which is the most suitable for any given purpose.

Masses for ground enamels are mostly composed solely of silica, borax and felspar, their fusibility increasing in proportion to the amount of the two last named, and it is possible, by varying the quantity of borax, to adjust the fusibility of the mass within a comparatively wide range.

To decrease the fusibility of any mass, the fused materials are ground and mixed with a known quantity of finely levigated clay, the amount of this constituent being so large that the powdered mass, when applied to the surface to be enamelled, can only be made to sinter or frit, without actually fusing. Ground silica or felspar may be used in place of clay, but in such event the mass will be transparent instead of opaque, both these bodies consisting of small particles of transparent material.

To render a mass more fusible it is either mixed with lead oxide or a large proportion of borax is taken, this modification being of course made when compounding the mass from the raw materials.

When the enamels are to be coloured, the addition of lead oxide must be made with great care, because many pigments will not develop their colour in presence of this substance. In such event it is easy to increase the fusibility of the product by the aid of borax.

The effect of magnesia is to render the enamel more readily distributable over the surface to which it is applied, and the use of this substance is therefore particularly advisable when preparing enamels desired to distribute uniformly on small articles.

A very important point in the preparation of all enamels is the so-called decoloration by means of oxidising bodies, added in order to convert ferrous oxide into ferric oxide, and thereby diminish the pigmentary power exerted by the former It is evident that the sole object accomplished by this treatment is the production of enamels with a yellow tinge, but not perfectly colourless, the sole means of effecting this latter desideratum being the use of perfectly pure and therefore costly, raw materials

There is, however, a simple means whereby enamel masses from somewhat impure materials can be obtained of a fine white colour, and this is by the addition of very small quantities of fine smalt to the mass Like all cobalt preparations, smalt is capable of imparting a deep blue colour to glass, but the shade in this case is complementary to the yellow tinge produced by ferric oxide, and therefore the one counteracts the other, the result being to leave the enamel quite white.

Of course this mutual destruction of colour only occurs when the right proportion of the two pigmentary bodies is hit upon, for if an insufficient amount of smalt be taken, the yellow from the iron is only weakened and still remains apparent, whilst an excess of smalt imparts a bluish (milk-white) tinge to the mass

The expense of decolorising enamels in this way is a negligible factor—a minute quantity of smalt sufficing for a large batch of enamel mass All that is necessary is to accurately determine, by several tentative experiments, how much smalt is actually required to produce the desired effect.

The colour of the cobalt pigments being unaffected by temperature, decolorising by smalt can be practised with the most refractory enamels, and is an operation that should never be omitted, beauty of appearance increasing the commercial value even of enamels for purely technical purposes.

XVI.

COMPOSITION OF MASSES FOR GROUND ENAMELS.

The ground enamels are those intended for direct application to metallic surfaces and, when applied and heated, must assume a state of semi-fusion (frit), so as to form a backing or foundation for the cover enamel.

The following recipes may be advantageously followed in preparing such ground enamel.

Very Refractory Ground Enamel Mass No. 1.

Fused together	Quenched and ground flint	30 parts.
	Borax*	20 ,,

To the fused mass is added, during grinding, about 25 to 40 per cent. of flint meal and an equal quantity of white clay, the fusibility varying in indirect proportion to the content of the material in these two substances. Ground felspar may be employed to replace the added flint meal.

Very Refractory Mass No. 2.

Flint meal	30 parts.
Borax	16·5 ,,
White lead	3·5 ,,

fused and ground along with—

Flint meal	25 to 40 parts.
Clay	20 to 25 ,,
Magnesia	5 to 6 ,,

---

* Crystallised borax containing 47·1 per cent. of water. When dehydrated borax is used, the quantity must be correspondingly reduced.

Owing to the presence of magnesia this mass is more refractory than No. 1, but is superior to the latter in many ways, being much easier to apply, and adhering strongly to the superior-imposed cover enamel.

Refractory Mass No. 1.

Flint meal	50 parts.
Borax	30 ,,

fused together and ground along with—

Silica	13 ,,
Clay	13 ,,

Refractory Mass No. 2.

Flint meal	50 parts.
Borax	30 ,,

fused together and ground with—

Silica	15 ,,
Clay	13 ,,
Magnesia	1 part.

Fusible Mass No. 1.

Flint meal	30 parts.
Borax	25 ,,
Felspar	30 ,,

fused together and ground with—

Clay	10·75 ,,
Felspar	6·00 ,,
Magnesia	1·25 ,,

Fusible Mass No. 2.

Flint meal	30 parts.
Borax	18 ,,
White Lead	3 ,,

fused together and ground with—

Flint meal	9·5 parts.
Clay	8·25 ,,
Chalk	2·00 ,,
Magnesia	0·90 ,,

Felspar-Lead-Oxide Mass of Medium Fusibility.

Flint meal	30 parts.
Felspar	30 ,,
Soda *	12 ,,
White Lead	3 ,,
Borax	15 ,,

fused together and ground with—

Felspar	6·25 ,,
Clay	11·75 ,,
Magnesia	0·75 part

Ground Mass for Iron Utensils, No. 1.

Flint meal	30 parts.
Borax	16·5 ,,
White lead	3·0 ,,

fused together and ground with—

Flint meal	9 ,,
Clay	8·6 ,,
Magnesia	0·5 part.

Ground Mass for Iron Utensils, No. 2

Flint meal	30 parts.
Felspar	30 ,,
Borax	25 ,,

fused together and ground with—

Clay	10·75 ,,
Felspar	6 ,,
Magnesia	1·75 ,,

---

* Anhydrous soda.

Ground Mass with Magnesium Sulphate, No. 1 (for Iron Utensils).

Flint meal	20 parts.
Borax	9 "
Potash	1 part.
Magnesia	6 parts.
Magnesium sulphate	2 "

fused together and ground with—

Clay	2 "

Ground Mass with Magnesium Sulphate, No. 2 (for Iron Utensils).

Flint meal	30 parts.
Borax	10 "
Magnesia	4 "
Magnesium sulphate	2·25 "
Soda	1·75 "

fused together and ground with—

Flint meal	18 per cent. of weight of mass taken.
"	18 " " "

The foregoing recipes are used in the largest works and suffice perfectly for all purposes in the enamelling of cooking utensils, boiler tubes, etc. In order, however, to afford makers a means of rectifying certain imperfections manifested by enamels a brief notice of these and their remedies will now be given.

1. Ground mass readily chips off from the foundation. *Remedy:* Add magnesium sulphate.

2. Mass difficult to distribute on the metal and holds badly. *Remedy* Add a little magnesia, excess being avoided as it makes the enamel too refractory.

3. Mass too hard. *Remedy.* Add a little lead oxide or potash; or, better still, both.

4. Mass too fusible. *Remedy.* Increase proportion of clay and flint meal when grinding the fused mass.

Percentage Composition of Certain Ground Masses.

(Analysed by Vogelsang.)

No	Silica	Borax	Potash or Soda	Lead Oxide	Clay	Magnesia	Magnesium sulphate	Lime
1	66·01	14·58	—	4·18	14·47	0·75	-	—
2	68·62	17·27	—	—	11·11	—	—	—
3	68·51	16·72	—	—	13·70	1·07		—
4	59·66	14·61	4·75	-	19·00	1·13	-	0·55
5	64·02	15·40	—	4·05	13·45	1·30	—	1·78
6	56·87	8·30	11·96	2·62	19·00	0·78	-	0·47
7	57·55	13·65	2·90		5·75	17·25	2·90	—
8	66·66	9·50	1·79		12·90	7·17	1·98	—
Average	63·49	13·75	2·67	1·36	14·05	3·72	0·61	0·35

Hence we see that the proportions of the true glass-forming components (silica, borax, alkalies, lead oxide and lime) vary only between narrow limits, whereas the substances acting as covering material, *e.g.*, clay and magnesia, may fluctuate considerably.

When one has selected a certain ground enamel mass, the same should be adhered to and adapted, on the results of experiment, so as to meet the end in view. This course is better than continually flying from one mass to another, which involves a greater waste of time and labour than are consumed in working on and modifying a single ground mass until it acquires the properties desired.

XVII.

COMPOSITION OF COVER ENAMELS.

Chemically speaking, cover enamels are glasses made translucent or even quite opaque by the addition of tin oxide or other white opaque bodies. Since a principal requirement exacted of these enamels is that they must be readily fusible and distribute uniformly over the ground enamel when melted, the composition must be regulated so as to enable these conditions to be fulfilled.

For special reasons it is, however, important to keep their fluidity within certain bounds, since if a cover enamel be fused in a crucible, and, after continued heating, left to re-cool, a peculiar result will be noticeable, *viz.* that while the mass at the bottom of the crucible is still pure white the intensity of the colour diminishes towards the top, the upper layers having the appearance of faintly turbid glass and being unsuitable for use as enamel.

The cause of this is not far to seek, being due to the high specific gravity of the tin oxide, which therefore settles down to the bottom of the liquid mass and leaves the upper portion almost free. Consequently, if the enamel is too fluid, it will not yield a homogeneous product, whether the opaque material employed be tin oxide or the cheaper lead oxide often used in place of the former.

In this connection bone ash acts in a very favourable manner, as, by reason of its low specific gravity, it does not settle down even in extremely fluid enamels, and is also cheap.

Only, when bone ash is used, it becomes necessary, in order to obtain a pure white enamel, to add to the mass a little saltpetre for the purpose of oxidising the carbon present, which is the cause of the grey colour of the ash. Lead oxide for producing opacity in enamels is rightly going more and more out of use, for though, when added to the fused and re-ground mass for fusible cover enamels lead oxide can by careful firing be preserved in an unfused and uncombined condition and therefore causes the mass to appear white, the colour is always tinged with yellow from the oxide and is never pure white unless an addition of smalt be made, which greatly contributes to the compensation of the colour. Moreover, the use of lead is inadvisable in enamels for technical purposes, the main object in which case is to obtain a product capable of withstanding chemicals, whereas a simple experiment will show how easily enamels containing lead oxide can be corroded by such agencies.

Thus if an egg be beaten up in a vessel lined with a cover enamel containing lead oxide, and left to stand in it for a day a brownish-black stain of lead sulphide will be found at the place where the egg has come into contact with the enamel, the small quantity of sulphuretted hydrogen liberated from the egg being capable of modifying the lead oxide in the manner described. Again when weak vinegar is boiled in a similarly enamelled vessel for a short time, the enamel will lose its lustre and become rough, while an appreciable amount of lead will be detected in solution in vinegar.

Consequently as lead is a very poisonous metal, buyers of enamelled utensils are perfectly justified in refusing ware coated with lead oxide enamels. Less objection applies to the presence of lead silicate as a constituent of the vitreous matter of the cover enamel, lead oxide being less readily dissolved out of this combination.

It must therefore be regarded as a welcome advance in the enamel industry that makers are for the most part discarding the use of lead oxide both for ground and cover enamels. The ware, though perhaps less handsome in appearance, is more indifferent to the action of chemicals, and even weak acids can be boiled in vessels coated with leadless enamels without effecting much corrosion.

With regard to the smelting of the mass for cover enamel, this has been sufficiently discussed when treating of the same operation in connection with ground enamel, the only difference being that the former require to be re-melted more often in order to get rid of all air bubbles. The rules already given for correcting defects also apply in the case of cover enamels, and may be amplified by the following:—

If the mass when solidified is not pure white but looks turbid and milky, whilst it is so far transparent that black pencil lines can be seen as grey streaks when viewed through a thin layer of the enamel, the content of covering material is insufficient and a small quantity of tin oxide or bone ash must be added to the pulverised mass before re-melting.

When the enamel is deficient in lustre it may be rectified by substituting soda for part of the borax.

If the enamel "crazes," or becomes intersected with innumerable fine cracks shortly after firing on the metal, it evidently contracts too much on cooling. *Remedy:* Increase the proportion of ammonium carbonate The reason why this very volatile salt influences the durability of enamel is unknown. It is, however, certain that it prevents crazing, and, consequently, ammonium carbonate is a substance employed in all enamel works.

Should the cover enamel fail to adhere properly to the ground layer an addition of magnesium sulphate will afford a remedy.

Excessive fluidity, and the consequent insufficient cohesion of the mass, can be corrected by the aid of magnesia.

The recipes for cover enamels are far more numerous than those for ground masses. The manner in which the formulæ should be modified depends in either case on the purpose for which the product is intended.

RECIPES FOR COVER ENAMELS

The recipes given below have proved thoroughly reliable in practice.

Leadless Cover Enamel for Cooking Utensils.

Flint meal	37·5 parts.
Borax	27·5 ,,
Tin oxide	30 ,,
Soda	15 ,,
Saltpetre	10 ,,
Ammonium carbonate	7·5 ,,
Magnesia	7 ,,

fused together and ground with

Flint meal	6·12 ,,
Tin oxide	3·66 ,,
Soda	0·70 part
Magnesia	0·70 ,,

In nearly all enamel works it is customary to store the mass, when ground, in a moist state, in suitable drums or casks with close-fitting lids

Plumbiferous Cover Enamel No. 1.

Silica	75 parts
Borax	48 ,,
Tin oxide	50 ,,
White lead	30 ,,
Soda	22·5 ,,
Saltpetre	20 ,,
Ammonium carbonate	15 ,,
Magnesia	10 ,,

fused together and ground with—

Flint meal	12·6 ,,

Plumbiferous Cover Enamel No 2.

Flint meal	88 parts.
Borax	50 ,,
Tin oxide	55 ,,
White lead	15 ,,
Soda	25 ,,
Ammonium carbonate	15 ,,
Saltpetre	22·5 ,,
Magnesia	12·5 ,,

fused together and ground with 12 to 20 parts of flint meal according to the degree of fusibility required.

Felspar Cover Masses

	I	II	III.	IV.	V	VI	VII.	VIII
Felspar	10	27	40	30	20	30	37·5	40
Borax	34	28	28	20	26	35	40	35
Tin oxide	15	20	8	14	13	20	25	26
Saltpetre	6	—	1·5	5	1·5	14	15	8
Ammonium carbonate		3	—		—	—	—	—
Magnesium sulphate		6	—	—	—	—	—	—
Magnesia	—	8	—	5	—	7·5	7·5	5
Clay		2		—	—	5	10	—
Soda	—	—	10	7	12	18	20	13
Flint meal		10			15	10	25	—

The foregoing felspathic cover enamels exhibit the advantage of being free from any insalubrious materials and of being ready for use, without any further addition when ground Should any of them prove too refractory, this defect can easily be remedied by adding a little borax in the grinding. When any other inconvenience is experienced the means already specified will be found suitable to correct the properties of the mass in the direction desired

Cover Masses containing Glass and Porcelain

Formerly little disposition was evinced in the direction of using ground porcelain or glass in compounding cover enamels, the products usually being insufficiently adherent or "too poor". However, since the discovery that the properties of enamel could be modified by adding other materials in grinding or re-melting the mass, glass and porcelain have attained considerable value as adjuncts, porcelain, in particular, being highly prized on account of its resistance to chemical agencies. A few recipes for masses containing ground porcelain and glass are given below.

Cover Masses containing Glass or Porcelain

Flint meal	25 parts
Porcelain	25 ,,
Borax	25 ,,
Tin oxide	20
White lead	20 ,,
Soda	15 ,,
Saltpetre	11 ,,
Ammonium carbonate	7.5 ,,
Magnesia	6 ,,
ground with	
Flint meal	6 ,,
Tin oxide	3.75 ,,
Soda	0.75 part
Magnesia	0.80 ,,

If the mass appears too opalescent (translucent) add 10 to 15 parts of tin oxide

II

Silica	20 parts
Powdered glass	20 ,,
Borax	24 ,,
Tin oxide	16 ,,
White lead	3 ,,
Soda	10 ,,
Saltpetre	2 ,,
Magnesia	5 ,,
Flint meal	6 ,,
ground with—	
Tin oxide	4 ,,
Soda	1 part
Magnesia	1

Other recipes, with a variety of combinations, are known, a few of which, furnishing really good results, are subjoined :—

	III	IV	V.*	VI.	VII
Flint meal	20	26	18	22	20
Glass .	20	26	18	22	20
Porcelain . .	—	—	—	—	—
Borax .	22·5	40	26	30·5	26
Tin oxide	20	29	19·5	22	20
Soda . .	5	—	—	3·5	2
Potash .	—	—	0·5	—	—
White lead	—	—	—	—	—
Saltpetre . .	10	11·5	9	10·5	10
Chalk	—	—	—	—	5
Lead oxide	5	—	—	—	—
Magnesia	5	7·5	5·5	5	5
Clay .		4	2·5	—	—

The following additions are made in grinding :—

To	III	IV	V. and VI	VII
Flint meal	16 per cent.†	18 per cent	1·8 per cent.	3·5 parts.
Borax	9 ,,	9 ,,	—	3·5 ,,
Magnesia	5 ,,	5·25 ,,	1·8 ,,	0·8 part.
Boric acid	—	1·5 ,,	—	—
Soda . .	—	—	1·0 ,,	0·8 ,,
Porcelain	—	—	—	3·5 parts.

	VIII	IX	X	XI	XII.	XIII
Flint meal .	25	25	—	—	—	—
Glass .	25	25	11	10·5	—	—
Porcelain	—	—	11	9	37·5	37·5
Borax	33·5	34	18	13·5	20·5	22·5
Tin oxide .	20·25	25	12	9	20	22·5
Soda . .	2·5	4	—	—	7·5	10
Potash .	—	—	—	—	—	—
White lead	—	—	—	—	—	—
Saltpetre	12·5	12·5	8	4·5	7·5	10
Chalk	6·25	6·25	—	—	—	—
Lead oxide .	—	—	—	—	—	—
Magnesium sulphate .	—	—	—	1·5	5	15
Magnesia .	6·25	6·25	4	3	12·5	12·5
Clay .	—	—	—	—	—	—
Ammonium carbonate .	—	—	—	1·5	—	5

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* These are particularly suitable for enamelling cooking utensils.

† Per 100 parts of fused mass taken.

Additions on grinding:—

To	VIII	IX	X	XI	XII	XII
Flint meal	4·5	10	3·8	30	34	13·5
Porcelain.	4·5	10	—	—	—	
Borax	4·5	10·75		—	—	—
Soda	0·9	—	—	4·5	—	—
Magnesia	2·5	3·5	4		5	3
Ammonium carbonate	—	1	—	—	4	—
Tin oxide				10	17·5	9·75

The foregoing recipes will suffice for every possible case. To modify any current formula for a special purpose is in most cases merely a matter of changing the proportions of one or other of the ingredients, bearing in mind the following considerations:—

1. Reducing the amount of borax decreases the fusibility of the enamel and *vice versâ*.

2. Increasing the proportion of borax lowers the power of resisting corrosion.

3. An addition to the percentage of tin oxide increases the opacity and whiteness of the mass, but diminishes its durability.

4. The use of lead oxide greatly increases the corrosibility of the enamel, and for this reason plumbiferous enamels should never be employed for cooking utensils.

5. White lead or potash softens the mass, whilst soda heightens its lustre.

The most important technical use for enamels is for the coating of cooking utensils and boiler tubes, in both cases less stress is laid on refractory character than on hardness—and, for cooking utensils, lustre. Consequently, large additions of lead preparations are generally avoided, nor is a certain limit exceeded for tin oxide, even though the colour comes out somewhat translucent instead of pure white like porcelain.

Although bone ash is procurable at very low rates this material does not, as yet, occupy the position it deserves in the enamel industry—the chief reason for which is apparently that, even when used in large quantity, it never produces so white an enamel as tin oxide, the colour having always a bluish-grey tinge

XVIII

PREPARING THE ARTICLES FOR ENAMELLING.

Enamelled articles for technical purposes consist either of iron ware (cast or wrought iron) or, less frequently, of copper or brass utensils, and in order to enable the ground enamel to adhere to the metal and prevent it chipping off, the latter has to be prepared beforehand by a special treatment.

This is a very important matter, since if the operation is not carefully performed, even the best-made enamel may chip off in a very short time. Copper articles are much easier to prepare than those made of iron, and it is never necessary for the first-named metal to be made perfectly bright by dipping in a pickling bath (dilute acid), since the enamel can be applied direct, provided the articles are not greasy on the surface.

The peculiar brownish-red colour generally exhibited by copper ware is due to a thin layer of cuprous oxide, and when enamel is fused on such a surface it adheres strongly thereon cooling. This is owing to the behaviour of the acid substances (boric acid and silica) in the enamel mass, these being in sufficient quantity to combine with a certain amount of oxides on fusing, so that when enamel is melted on an uncleaned surface of copper the cuprous oxide is dissolved by the mass, which then adheres firmly to the metal.

If a piece of copper, covered for instance with white enamel, be examined by scraping off the enamel layer, it will be found that the stratum nearest the metal is of a greenish or reddish colour, due to the dissolving of the layer of oxide at the surface of the metal. If this oxide layer contained much cupric oxide, the adjacent enamel will appear bluish-green, whilst if chiefly cuprous oxide the colour will be of a reddish cast In order to obtain a pure white coating of enamel under these circumstances, the cover enamel must contain sufficient tin oxide to completely mask the ground layer; otherwise the colour of the latter will show through and affect the shade of the superior layer. Thus, copper can be enamelled without having been pickled, provided the expense of preparing such a cover enamel is not considered too high

The conditions are, however, totally different when the enamelling of iron is in question, since that metal is never chemically pure but is always combined with other substances. For instance, cast iron may be regarded as iron containing variable quantities of iron carbide, iron silicate, etc., in solution, and also embedded crystals of carbon (graphite) In cast iron also the outer layer or "casting skin" must be distinguished from the inner substance of the metal, exhibiting the above-named character. This outer skin consists of ferric oxide, and of particles of carbon derived from the mould in which the metal was cast -these moulds being dusted over inside with charcoal powder, before use. Small crystals of graphite also separate out in the external layer of the iron during cooling

Experience shows that only certain kinds of iron can be enamelled with ease, this property depending on the method pursued in making the cast iron. For example, iron that is drawn off from the blast furnace whilst still in an extremely hot (molten) condition, cools rapidly in the moulds and then forms the so-called "white" iron, which is distinguished by its steel-grey colour, great hardness, and by containing, in a very finely-divided state, all the carbon originally dissolved in the metal On iron of this kind enamels hold with great tenacity, and therefore it was formerly the practice to select articles made from this iron, or at least exhibiting a "white iron" surface, for enamelling.

If, on the other hand, the iron is not particularly hot when it leaves the blast furnace, and is cooled down gradually in the moulds, a considerable portion of the dissolved carbon crystallises out on the surface in the form of graphite, and such "grey" iron is difficult to enamel

Certain objections, however, exist against the use of white iron for utensils, chiefly on account of the extreme hardness and brittleness of this form of the metal, in consequence of which they are very easily cracked or broken under the influence of shock It therefore becomes necessary to make such utensils of iron that exhibits intermediate properties between the white and grey kinds, an object attainable by special precautions during casting, the iron being run, at a moderate heat, into perfectly cold moulds, the effect of which is to cool the surface of the metal very quickly so that this layer assumes the form of "white" iron, whilst the internal mass cools down more gradually into the condition of "grey" iron.

The difference may be noticed on examining under a magnifying glass a broken piece of some utensil that has been produced by casting in the above-named manner

Experience has shown that iron produced by smelting with coke is less suitable for enamelling than when wood charcoal has been used. In view of the importance of this matter the manufacturer of enamelled iron ware should therefore always endeavour to procure the utensils he has to enamel from iron-founders who employ iron possessing the above-mentioned qualities.

Apart from the properties of the iron used, the mode of casting the ware is also of importance. The walls of the utensils should be thin and of as uniform thickness as is possible; and the ware should be carefully examined, all pieces exhibiting air bubbles, pittings, flaws, etc., being rejected as unsuitable.

Before commencing to enamel the goods they must be subjected to a course of mechanical preparation, all projections (from the joints of the moulds, etc.) being removed by means of a sharp file so as to leave a perfectly smooth and uniform surface

CLEANING THE SURFACE OF THE WARE.

Articles with a surface of white iron can be enamelled at once after the foregoing mechanical preparation—all that is necessary being to scour the surface of the metal over with sharp sandstone or pumice until perfectly bright If not enamelled immediately, they must be stored away from contact with dust or moisture; but as iron of such perfect quality is rarely encountered, and as all other kinds require chemical treatment before they are fit for the enameller it is usual to make no exception and to treat all articles in the same way, *viz.*, by pickling

PICKLING

This operation consists in dipping the goods in a liquid capable of dissolving away any superficial layer of oxide and leaving a perfectly bright surface of metal

At present the older forms of pickling material (vinegar, steeped barley grits, etc) are very rarely employed, having been almost entirely superseded by sulphuric acid As already mentioned, the usual strength of acid pickle is 1 part of commercial sulphuric acid to 20 to 22 parts of water, the time of immersion depending on the strength of pickle adopted. Thus, if the exposure is not to be more than ten or twelve hours, a stronger, moderately concentrated, acid must be used, but for slower working a weaker pickle is employed. As a rule the ware should not remain longer than twenty-four hours in pickle.

When the pickling liquor has been for a long time in use and has taken up a relatively large amount of iron into solution, the result of leaving the goods too long in the bath is that the liquor forms, in presence of the iron, certain insoluble basic salts which adhere firmly, as a soft powder, to the metal and defeat the object of the process. Such "over-pickled" goods must be scoured again with sharp sand and pickled afresh.

The pickling vats are generally made of hard wood, but as they are soon corroded and spoiled by the acid it becomes advisable to varnish them over inside and thereby protect the wood from contact with the acid liquor.

The higher the temperature of the pickle the more rapid its action; consequently the water used is generally warmed to 30° to 40° C., and the pickling room is kept warm to prevent the temperature of the liquor from falling. The scouring room for cleaning the pickled ware should be situated next the pickling room and should contain a rinsing vessel and a boiler, so as to provide a constant supply of hot water.

When sufficiently pickled, the utensils are taken out of the bath, rinsed in cold water, and turned over to the scourer, who scrubs them over with fine sharp sand (preferably quartz sand) until the surface to be enamelled is perfectly bright. In large works, simple mechanical appliances which perform the bulk of the work of scouring, in a very short time, may be advantageously resorted to, the final stages being always done by hand labour. The next step is to rinse the goods, in order to remove every particle of adherent sand, after which they are dried in a special manner, namely, by dipping them in hot water for a few seconds and then exposing them to the air, whereupon the thin stratum of (nearly boiling) water is immediately evaporated by the heat of the metal.

When dry, the goods are quite ready for enamelling, and should, preferably, be handed over at once to the workman entrusted with that task. If this is inconvenient they must be stored out of contact with dust. Attempts have been made to store the pickled and rinsed ware under water, but when well water is used it is found that the bright surface very soon tarnishes and becomes covered with a yellow sediment. This is due to the presence, in well water, of carbon dioxide, which corrodes iron, the free oxygen, also invariably present, converts the dissolved ferrous oxide into ferric oxide, which is thereupon deposited as firmly adherent rust—very difficult to remove.

The best plan to adopt in all instances is to arrange the various operations in the works, so that the goods when pickled and dried can be immediately handed over to the enamellers

XIX.

APPLYING THE ENAMEL.

The work of enamelling is always divided into four operations, namely, applying the two coatings of (ground and cover) enamel and firing the same. In themselves these tasks are all very simple and apparently easy to carry out. In reality, however, their performance requires the aid of skilled and experienced workmen, otherwise a large percentage of defective pieces will be produced difficult under the most favourable circumstances, to work up afterwards into ware of good appearance.

APPLYING THE GROUND ENAMEL.

The masses for ground enamel are generally stored damp, when ground, and in this condition usually have the consistency of thick honey or sometimes that of soft cheese.

To impart the necessary fluidity to the mass a portion is taken up in a ladle of enamelled iron, out of the storage vessel, and poured into a pan where it is reduced, by the addition of water, to a thick cream which must be stirred until perfectly homogeneous and free from lumps or excessive thinness in places. The best way to attain this end is by adding the water in small quantities and stirring it in continuously.

The ware to be enamelled is heated in a drying oven to about 40° C., so that the pieces can still be handled without inconvenience; this warming-up is necessary to facilitate the adhesion of the enamel mass.

The enamel is applied in the following simple manner: The workman takes the warmed utensil from the oven and lays it on an adjacent table; he then stirs the enamel mass up well, dips a stiff brush into it, and, by means of a ladle, takes out of the pan and pours into the utensil as much of the dilute mass as he thinks will about suffice to form a coating. By means of the brush this is then distributed over the inner surface of the article, uniformity of distribution being facilitated by tapping the piece with a wooden mallet. Finally the piece is laid, mouth downwards, on a couple of horizontal supports, placed over the enamel pan or over another vessel to catch the drippings, or excess of enamel.

Highly-skilled enamellers dispense with this last operation altogether, long practice enabling them to judge precisely the quantity of mass required to coat a utensil of given size, so that no excess remains to be drained off.

When drained, the piece is set on the table and the enamel carefully wiped away from all parts that are not intended to be coated; after which it is immediately transferred to the drying room.

The drying arrangements in enamel works are generally very defective, but little of the heat from the drying ovens being utilised. A very useful plan is to fit up the drying room with racks, which can be raised by degrees nearly up to the ceiling—the freshly enamelled pieces being placed on the rack in its lowest position, and afterwards gradually lifted to enable the ware to dry rapidly and equally. Only when it is certain that the mass is perfectly dry is the rack transferred to the drying oven, which is heated to nearly red heat in order to expel the final traces of moisture from the mass.

Uniformity in drying is of special moment in ensuring the success of the entire operation, since if the ware is put in a hot place before being perfectly dry, the enamel easily separates from the metal, and the ware will need re-touching to produce a proper coating.

Only after the ware has stood for some time on the nearly red-hot plate of the drying oven will the powder have become so adherent to the metal as to require the exertion of some force to scrape it off by means of the finger nail, and when this stage is reached the ware is ready to be fired

XX.

FIRING THE GROUND ENAMEL.

Firing consists in heating the coated ware sufficiently to produce incipient fusion of the granules of the enamel mass, without, however, causing them to run together into a perfectly uniform mass, so that the process is really more one of sintering than true fusion.

The ground mass may be fired on to the ware by suspending the latter over a bright fire of wood, charcoal or coke, until the necessary degree of heat is attained. These fuels are, however, attended with the disadvantage of giving off particles of flying ash, which are carried along by the gases, the reducing action of the gas also corroding the enamel mass. Consequently, to obviate these inconveniences, the firing of the ware is always performed in muffle furnaces.

THE MUFFLE FURNACE.

The construction of these furnaces is very simple. They consist of an ordinary furnace fitted with prismatic vessels (muffles) of fireclay, which are enveloped by the flame, the furnace itself is connected to a chimney able to produce a strong draught, and is capable of furnishing very high temperatures.

The usual method of regulating the fire in these muffle furnaces is such that the front surface of the muffle is heated less strongly than the back, the latter being brought to a strong red heat, whereby the enamelled ware can be exposed to a higher or lower temperature at will. A muffle of the usual type met with in enamel works is shown in Fig. 14.

Here O is the furnace, M the muffle, R the hearth, A the ashpit, B the stoking hole for introducing the fuel and P the plate for charging and emptying the muffles.

It will be easily understood that muffles of different sizes will be required in enamelling works. Nevertheless, it is desirable, in order to prevent unnecessary consumption of fuel, to use muffles only just large enough to contain the ware to be fired. To prevent undue cooling of the hot air in the muffle, the front end is closed by a plate of suitable dimensions, provided with a peephole, either open or covered with mica. The space in front of the muffle is also provided with a hot plate to accommodate the pieces before and after firing.

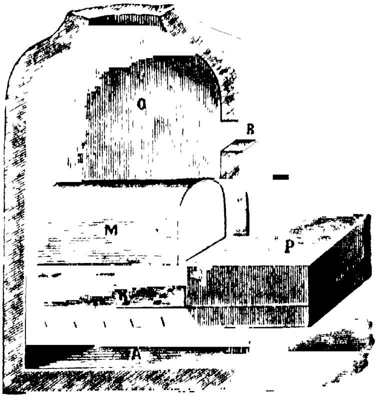

FIG. 14.

Before commencing to charge the muffle it must be raised to cherry-red heat inside, the rear being then almost pale red. The size of the muffle depends on the skill of the workman in charge of the firing, an experienced man being able to look after twelve to fifteen small utensils in the muffle at a time. Care should be taken, when charging the muffle, to arrange the pieces in such order that each of them can be moved about to a hotter or cooler position as required.

For shifting pieces fitted with handles a simple fork is used, which engages with the handles when the ware is to be moved, whilst other utensils are handled with tongs of suitable shape.

The ware is inserted first in the cooler part of the muffle, and afterwards pushed gradually onward to the hotter parts. Flat pieces, such as basins, stewpans, etc., may be set upright on the bottom of the muffle, whereas taller articles, after the enamel on the bottom is fused, must be laid down sideways, and turned round so as to bring the enamel on the sides into a state of fusion

The operation of firing ground enamels should not take longer than twenty to twenty-five minutes at most, in a well-heated muffle If not properly fired in this time, the enamel mass is evidently too refractory, to remedy which defect a certain quantity of calcined borax or boric acid can be mixed in with the diluted enamel by prolonged stirring. If this does not produce the desired result nothing else can be done but to add borax to the mass and fuse it over again

In view of this possibility it is always advisable, before preparing a new batch of ground enamel mass in large quantity, to test it by making up a small trial batch and testing same in the muffle.

As a practical sign that the ground mass has been properly fired, the best indication is that it cannot be rubbed off by the fingers. When examined by a strong magnifier, the edges of the individual particles should appear rounded, in which event the mass has attained the requisite degree of fluidity, being "fritted" and not really fused

If, on the other hand, the mass assumes the appearance of a smooth lustrous covering on the surface of the ware, this is an indication of excessive fusibility. In this case the ground mass forms, in itself, an enamel, and the firing of the cover enamel is then attended with difficulties. This defect may be corrected by an addition of some refractory substance, such as flint meal, porcelain sherds or clay, all of which are very serviceable.

The temperature usually requisite for firing ground enamels should not exceed pale red heat and it is but rarely that, for firing extremely refractory masses, the employment of a white heat is entailed. Articles enamelled with the latter kind of mass are naturally dearer than those coated with fusible enamels, owing to the greater outlay on fuel.

When large pieces have to be treated, or such as have been already enamelled but are damaged by long usage, a somewhat modified method is pursued. Old cooking utensils, from which the enamel has chipped off in places, must be hammered with a pointed hammer round the defective parts to remove all loose pieces of enamel, and then exposed to strong heat to completely destroy all the adherent fat almost invariably present. The exposed portions of metal having been scoured bright are then coated over with ground mass and fired in the muffle as usual.

To enamel large pots, boilers etc. they must be filled with pickling liquor and afterwards scoured bright, painted over with ground mass, and fired in large muffles. In all cases the enamel must, before firing, be carefully wiped off any parts not intended to be covered. Utensils of special shape, particularly those with walls of irregular thickness, must be handled with extreme care in the firing and should be left in the muffle until it is perfectly certain that the mass is properly fritted all over.

GAS MUFFLES.

The employment of gas for heating is attended with so many advantages, and offers such a great saving of fuel, that it can be strongly recommended for all purposes where warmth is required in enamelling works.

So-called "water gas" is the best form to use. It consists of carbon monoxide and hydrogen, and furnishes such a high calorific effect that the fusing of enamels by the aid of this fuel is a very rapid process.

Gas is also of most excellent service in heating muffle furnaces, as it enables the temperature of the muffles to be regulated to a nicety, according to requirements. A muffle furnace of this description, the invention of the author, is represented in Fig. 15.

This furnace contains two superimposed muffles, *E* and *V*, of equal size, made of strong boiler plate. The upper muffle, *V*, serves for warming up the ware, whilst the enamel is fired in *E*. The muffles are enclosed in a thick casing of fire-bricks held together by dowels, and the whole is mounted on a strong iron baseplate, a narrow space being left between the muffles and the outer casing. Gas is supplied from the pipe, *G*, to a horizontal pipe bent in the form of a *U*, on which Bunsen burners, *B*,*B*, are mounted, at intervals of two inches, along the full length of the muffle. By means of a central partition, *W*, the flame from the two rows of burners is deflected right and left respectively. The burners are lighted through suitable lateral openings, *O*, which are then closed by means of earthenware plugs.

The flames surrounding the muffle *E* on all sides heat this white hot in a few minutes, and the gases escaping into the upper part of the furnace are still so hot that the muffle *V* is soon brought to red heat. The hot gases discharged through

S are conducted away for drying the products of the stamping mills, etc.

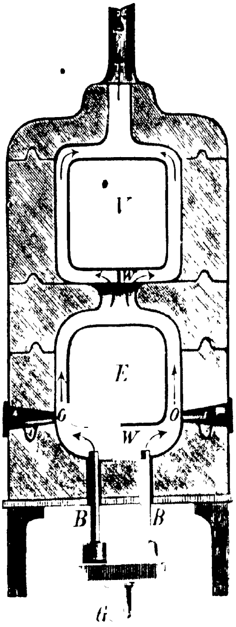

Fig. 15

When the apparatus has been in work a short time, the utensils in *V* will have become so hot that a very brief sojourn in *E* suffices to suitably fuse the enamel mass.

XXI.

APPLYING AND FIRING THE COVER ENAMEL OR GLAZE

When the utensils are taken out of the muffle in which the ground enamel has been fired on, the uncovered parts of the metal will be found covered with black, or magnetic oxide of iron resulting from the action of oxygen on the glowing metal. As this layer of oxide easily falls off and will colour any cover enamel it touches, it must be carefully removed before the covering mass is applied This operation is best effected by scrubbing with steel-wire brushes, or sand-paper. The application of the diluted cover enamel mass is performed in the same way as in the case of ground enamel, the extent of dilution having been determined by a preliminary experiment as the thinner the layer the handsomer and more durable the enamel The covering layer must, however, be thick enough to cover properly, and therefore, when the mass is rich in tin oxide, it can be diluted to a greater extent than otherwise feasible Bone ash has less covering power than tin oxide, and consequently a mass containing the former must not be thinned down so much as if the latter body were present. When the use of very dilute covering masses is necessary, the greedy absorption of the contained water by the porous ground layer entails great care in drying the ware before firing; otherwise the escape of steam from the ground enamel will produce defects in the upper layer.

Much greater care on the part of the workmen is required in firing cover enamel than in grounding, since the enamel must be perfectly free from bubbles, any pieces faulty in this respect having to be set aside and touched up again.

The firing temperature of the muffle furnaces is lower when cover enamels are being treated, these masses being of a more fusible character than ground enamels. An accurate indication of the proper degree of heat can be gained by placing a small crucible, containing a little brass, in the muffle, which will be hot enough for our present purpose when the brass fuses. Owing to the fluidity of the cover mass and its consequent liability to run down the sides of the utensils and make the coating unequal, the articles in the muffle must be frequently turned and laid on their sides in order to facilitate uniformity of fusion

As soon as the mass appears to have fused completely, the ware is taken out of the furnace, but is prevented from cooling down too quickly or the enamel will craze through lack of time for uniform contraction To prevent this, the finished ware is transferred to a muffle furnace, kept at a gentle red heat, where the pieces are piled up, and the muffle is then closed and left to cool down gradually It is advisable to employ for this purpose a large muffle so that as many pieces as possible can be treated at a time Under these circumstances the muffle need not be more than moderately hot, the radiant heat from the large charge of ware sufficing to raise it to the right temperature.

When cooled the ware is either blacked, nickel-plated, or —as is now most general—enamelled on the outside. This latter operation is performed in the same manner as before, except that commoner ground and cover masses, requiring less heat in firing, are employed. As coloured enamels (dark blue, coloured by cobalt, or red brown, by ferric oxide) are mostly used for this work, the ground mass is generally of low quality, made from impure materials and showing a yellowish or reddish tinge of colour.

If not enamelled on the outside, the ware is usually blacked over to prevent the appearance being spoiled by rust; and, with this object is painted over with coal tar applied while

XXII

REPAIRING DEFECTS IN ENAMELLED WARE.

In producing enamelled ware on a large scale it must happen, despite every care, that a certain percentage of the goods are defective and unfit for sale. A short description of these defects will now be given.

So long as the enamel mass is still glowing, it is of a handsome yellow colour, which gives place to a white—that should be perfectly pure—when the piece cools down. If, however, at this stage, the enamel exhibits an irregularity of surface, with dark, dull specks, it indicates imperfect firing, and therefore the ware should be at once replaced in the hottest part of the muffle to enable it to attain the requisite temperature.

When the goods have been overheated in the muffle, the first indications of this defect only make their appearance after the pieces are quite cold. In such event the enamel shows up very thin and blistered in places, and it not infrequently happens that the enamel and ground mass fuse together, and chip off so completely as to leave the bright metal exposed. This is due to excessive contraction of the fusion-product of the two masses, in consequence of which it tears away from the metal in cooling.

The only feasible way to rectify ware that has been overfired is to chip off all the defective enamel with a sharp-edged hammer, and to coat and fire the exposed surface anew with ground and cover enamel. As this is a very troublesome process many makers are content to merely apply and fire a fresh layer of cover enamel on the damaged surfaces, and sell the goods as second-class ware.

Apart from the question of commercial morality several reasons may be urged against such a practice. For instance, the "outshots" or second quality goods must always be sold at much lower prices than perfect ware, although they really cost the maker more to produce. Moreover, it cannot add to the credit of any maker to be continually offering large quantities of second-rate goods. Consequently, endeavour should always be directed to restricting the number of articles that require touching up, and any that have to be made good should be dealt with in such an effective manner that the corrections cannot be detected

For this purpose it is important to employ properly taught workmen for the task of firing the ware, and these men should be thoroughly well acquainted with the properties of the enamel masses generally used in the works. When new masses are to be employed, the qualities of which are, as yet, undetermined, they should be subjected to an experimental firing test made in presence of the workman who will have to fire the mass when in use, since he will often be able, in watching the progress of the operation, to obtain an idea of the behaviour of the mass from its appearance while in a glowing state.

Chemical Examination of Fired Enamels.

As already mentioned, the value of an enamel mass for technical purposes mainly depends on its capacity for resisting physical and chemical influences. It is therefore important that a maker should be in a position to apply simple tests to the enamel, with this object, to enable him to recognise which enamels fulfil the requirements exacted by them, and which do not.

The chief physical influence to be resisted is that due to extreme fluctuations of temperature, and in this connection the enamel can be very easily tested by heating it quickly followed by rapid cooling, the simplest plan being to fill the enamelled utensil with water, raising this to boiling point, and then immersing the vessel in cold water The enamel mass, after this test has been several times repeated, should still exhibit its original characteristics without alteration, and no cracks should be visible.

The chief chemical influences to be resisted are acids and alkalies, and the enamel may be considered as sufficiently proof against the former if, when the enamelled ware has been filled with boiling vinegar for about a quarter of an hour, the liquid gives no precipitate on subsequent exposure to a current of sulphuretted hydrogen The absence of such precipitate indicates that the enamel has suffered no corrosion, the lustre should also remain unimpaired

A very simple test for the presence of lead in an enamel consists in moistening a portion of the enamel with strong nitric acid, to destroy the upper layer After rinsing the spot with water a drop of ammonium sulphide is allowed to fall on the place, whereupon, in the absence of lead, no change of colour will ensue, whereas, if lead be present, the spot originally occupied by the nitric acid will immediately darken and in a short time turn quite black. The opinion has already been laid down that enamels for cooking utensils should be free from lead, on account of the poisonous properties of that metal, the dangers of which are intensified when the superficial layer of enamel has become damaged or defective

XXIII.

ENAMELLING ARTICLES OF SHEET METAL.

Since the introduction of machinery for rapidly manufacturing articles from sheet metal by blocking, stamping, etc , many attempts have been made to enamel the goods so produced, since, by reason of their cheapness and lightness, such articles undoubtedly best fulfil all the requirements expected of utensils. The majority of these attempts, however, resulted only in failure, the enamel either chipping off the sheet metal or becoming so irregular when fired, that many makers began to look upon success as impossible

Nevertheless, though it cannot be denied that the enamelling of sheet-metal ware is attended with certain difficulties, a glimpse of any ironmonger's stock will show that these have been satisfactorily overcome, and that the trade in enamelled sheet-metal goods is continually increasing, whilst inquiries for enamelled articles of cast iron are becoming fewer.

As a matter of fact there is no fundamental difference in the methods of enamelling these two classes of goods; all that is necessary to attain success in treating sheet metal being to remember the divergent properties of the two varieties of the metal, and proceed accordingly

If a piece of cast iron and a piece of sheet iron be etched with acid, and the attacked spots examined under a fairly strong magnifying glass, a great difference between the behaviour of the two varieties of metal will be evident at the first glimpse. Cast iron is a body formed by gradual cooling from a fluid condition, the smallest particles of the molten mass were able to settle themselves freely, and crystals were formed; every cast iron exhibits crystalline structure, as may readily be seen by examining the surface of fracture when a piece of this iron is broken.

On the other hand sheet iron, as is well known, is produced by the continued rolling of wrought iron or blocks of Bessemer steel, in mills until a sheet of any desired thickness is obtained. In consequence of this forcible mechanical treatment, the structure of the iron (or steel) undergoes very considerable alteration, the original granular-crystalline structure being converted into a fibrous condition, that is to say, in place of the fine crystals we now find long slender threads.

The smooth surface of cast iron may be regarded as covered with innumerable projections corresponding to the surfaces of the individual crystals, whereas the surface of sheet iron may be represented as covered with a tangle of slender threads. Now it is evident that, in the former case more numerous points of attachment are presented to the enamel, which therefore holds more firmly than to the fibrous surface of sheet iron. In addition to this comes another consideration, *viz.*, that during solidification the smallest particles of cast iron assume the positions allotted to them by the law of crystallisation of this metal, and when the iron is heated, they simply move asunder, returning to their original place when cooled, always behaving in a uniform manner. Hence provided the coefficient of expansion of the enamel coating is in any way approximate to that of cast iron, there will be no danger of the enamel chipping off.

In sheet iron on the contrary, the individual particles of metal are never in the position they would have assumed had they—like cast iron—been free to make their own selection, they are rather in a condition of mutual tension, the extent of which is such that, as is well known, certain kinds of sheet metal cannot be rolled out to less than a given thickness without cracking.

When sheet iron is heated, the fibres of which it is composed expand more in a longitudinal direction than transversely. If, now, such a sheet be imagined as coated with enamel—which, being a fused mass, must exhibit uniformity of expansion in all directions—it will be evident that the cohesion between the metal and enamel is by no means so intimate as that between enamel and cast iron, and it is only by special treatment that sheet iron can be enamelled in such a durable manner as cast iron

The whole secret of this treatment consists in an endeavour to make the surface of the sheet iron as nearly as possible like that of cast iron, so as to present to the enamel an equal number of points of adhesion as offered by cast iron.

The preparation of cast-iron goods by pickling, filing, and scouring for enamelling has already been described in the preceding section, and though when the articles are enamelled at once the final scouring can be omitted in this case, the conditions are different when sheet-iron ware is in question. Here scouring with fine hard sand is an important operation and one that requires care in its performance, since it contributes greatly to the durability of the enamel coating. This result is due to the tiny furrows cut in the surface of the metal by the hard particles of sand (the medium fine meal from quenched quartz may be used in the absence of suitable sand). By this means the fibres of iron exposed by the pickling process are subdivided, and the surface of the metal is rendered more approximate to that exhibited by cast iron; the enamel is therefore better able to adhere.

The enamel masses intended for use on sheet-iron ware must possess the highest coefficient of expansion possible for vitreous substances, and every maker should endeavour to ascertain by experiment the most suitable mass for the iron, with which he has to deal, since the sheet metal supplied by different rolling mills exhibits divergent degrees of expansion.

The reason for the necessity of a high coefficient of expansion in enamels for such ware is not far to seek, and resides in the thinness of the sheet metal employed The walls of sheet-iron ware seldom exceed $\frac{1}{25}$th of an inch in thickness whereas the thinnest utensils of cast iron are twice or three times as thick Consequently a sheet-iron vessel, when heated, rapidly becomes hot all the way through, and therefore expands very quickly, hence if the enamel is unable to follow this movement it must necessarily tear away from the metal.

To counteract this inconvenience—as it must be regarded from the present point of view—of rapid conduction of heat, it is customary to enamel the utensils on the outside as well, the result of which treatment—enamels, as vitreous bodies, being bad conductors of heat—is to prevent the rapid heating through of the metal, and thereby to a certain extent protects the inside enamel from disruption.

Sheet-iron ware may be divided into two classes according to the methods of manufacture adopted, *viz.*, those made entirely out of a single piece such as very flat stewpans, and those wherein several pieces are joined together by lapping or riveting Those of the first class offer no special difficulty to the uniform fusion of the enamel coating, provided the metal is of the same thickness throughout, but lapped or riveted articles are harder to deal with and require very skilful handling in order to produce a good class ware free from a large percentage of "outshots."

This is due to the circumstance that the metal is much thicker at the lapped or riveted joints than anywhere else, which thicker places remain hot much longer than the rest when taken out of the muffle, and consequently the enamel there is still fluid after the remainder has become solid The result is that when the last portions of enamel set hard, tensions arise between the particles, and fine cracks are formed; these usually radiate from the rivets and in length exceed the diameter of the latter three- or four-fold. The same thing happens in the case of lapped joints, the cracks making their appearance on both sides of, and perpendicular to, the joint.

It was owing to the occurrence of these inconveniences that the production of perfect ware of enamelled sheet iron was so retarded as to be looked upon for a long time as impossible. There are, however, two very effective means of reducing the formation of the aforesaid cracks to a practically negligible minimum, the one consists in exerting the utmost care to make the enamel coating as thin as possible, whilst the second is to ensure very protracted and uniform cooling down on the removal of the ware from the muffle.

It will be readily understood that a very thin coating of enamel will be the better able to follow the expansion and contraction of the underlying metal the slower the cooling process is carried out, since in the latter case the vitreous coating acquires a comparatively high degree of elasticity, and consequently is enabled to better withstand rapid changes of temperature.

Moreover, it must not be forgotten that the durability of the enamel is always greatly increased when the cooling process is conducted gradually, the so-called "toughened glass" (*verre trempé*), which is so resistant that it does not crack when molten lead is poured into a cold vessel made of the material in question, is prepared by simply cooling the glass ware very slowly indeed.

From the explanation given above, the intelligent manufacturer, who does not shirk the trouble of instructing his workmen thoroughly, will find no difficulty in producing faultless enamelled sheet-iron ware. Furthermore, since in many works the iron ware is both manufactured and enamelled it is easy to make the ware in such a manner as to reduce the difficulties of enamelling to a minimum

For this purpose the thickness of the metal should be reduced, as far as consistent with safety, at the places where two layers have to overlap, *i.e.*, at the joints, so that the total thickness at the joint does not greatly exceed that of the single layer of metal elsewhere

For readily appreciable reasons only flat-headed rivets should be used, and the heads should be thinned down to the lowest possible dimensions

The ground enamels should be of fairly refractory character, those rich in felspar being the best for use on sheet iron; and for these no extremely high furnace temperature is required, all that is necessary to attain being a condition of fritting or sintering of the mass, in which state the individual particles, while adhering firmly to the metal, present a comparatively rough surface which fuses to a homogeneous whole with the subsequently applied cover enamel

The latter may be also somewhat refractory and must be applied with extreme care in order to keep the entire coating as thin as possible. Of course, in view of this essential condition, it is almost impossible to obtain an absolutely opaque enamel covering, and, moreover, experience has shown that enamels of such low covering power that the colour remains bluish or grey, are far superior in point of durability to those whereby the ground enamel is carefully concealed, the employment of the quantity of tin oxide necessary to secure this latter result decreasing the coefficient of expansion.

The firing of ground and cover enamels on sheet-iron ware necessitates great skill and should be carried out as quickly as possible. The best plan is to heat up the muffle for firing the ground enamel to strong white heat, and to introduce the ware in a red-hot condition. With this object a second muffle, kept only at a red heat, is provided near the actual firing muffle, and serves to warm up the ware. The course of the operation is then as follows:—

The workman charges the heating-up muffle with a number of pieces of ware, in such a manner that any piece can be easily taken out and replaced in its original position. When a piece has attained to dark red heat it is quickly transferred to the firing muffle, where the fritting of the mass is rapidly effected, since the ware only needs a very little extra heat for this result to ensue, and the operation will be complete in a few minutes The piece is then returned to the heating-up muffle and its place taken by another. As this last-named muffle does not require to be heated very strongly it may be of large dimensions, and fitted with racks or shelves in order to utilise the whole of the internal space When a number of pieces have been coated with ground enamel and fired as described, they may be left to cool slowly in the heating-up muffle or transferred to a moderately hot cooling (annealing) oven for this purpose The heat radiated by the ware will suffice to heat up this oven to the requisite temperature, and the cooling process will go on with the necessary slowness.

The next stage is the application and firing of the cover enamel. This is effected in the ordinary manner and the firing and cooling are carried out in the hot muffle and cooling oven respectively. As the muffle is kept at a very high temperature, while the cover mass is not difficult to fuse, three to five minutes are generally sufficient to complete the firing.

If left too long in the hot muffle the fused cover enamel becomes very fluid and runs down from the sides of the ware to accumulate at the bottom. The result is that the walls, being only thinly covered with enamel, look grey, whilst the bottom shows up pure white where the enamel has gathered in thicker patches, and it is here that, by reason of the extra thickness, that the enamel exhibits the greatest tendency to chip off.

To improve the appearance and durability of the ware it is generally enamelled outside as well as in, but with less refractory masses, and coloured either blue (with cobalt) or brownish red (with ferric aluminate) For the reasons already given, the outside coating should be as thin as possible, though naturally greater care is bestowed on the finish of the inside

By following the instructions already given, any manufacturer will be able, after a little experimenting, to produce highly uniform and durable enamelled sheet-iron ware, and, given a little experience, it is not difficult to enamel very large utensils properly, since the sheet-iron goods are much easier to handle in the muffle than the heavier cast ones.

Latterly, boiler tubes of riveted steel plate have been enamelled, and specimens of such tubes exhibiting the most satisfactory qualities are in existence Of course, the production of this class of goods necessitates the laying down of special plant for firing the enamels, and the muffles have to be correspondingly long. As particular skill on the part of the workmen employed in the firing is requisite, the production of these tubes forms a special branch of the enamel industry

XXIV.

DECORATING ENAMELLED WARE.

The beginning of attempts at decorating enamelled ware consisted in covering the outside with blue or red-brown enamel or by nickel plating

GRANITE WARE.

The appearance of granite is produced on the outside of this ware by first coating it with white or yellow enamel and then spraying it over with very fine drops of a fusible greyish-blue or greyish-red cover enamel greatly diluted with water, kept continually stirred whilst the spraying is being effected in order to maintain uniformity of strength. When the drops are dry and the ware is fired, the cover enamel adheres firmly to the ground layer and produces the appearance of granite. The look of the goods is greatly improved by a thin final coating of very fusible cover enamel or glaze.

TRANSFER DECORATION.

Since the introduction of enamelled iron table and chamber ware—plates, saucers, jugs, wash-basins, etc.—the necessity for further decoration has arisen; but as cheapness is an essential factor, hand-painting is out of the question for such ware, and recourse has to be had to the same means as are so successfully employed in the manufacture of porcelain and stoneware, *viz.*: decoration by the aid of so-called transfer pictures.

This process chiefly consists of printing coloured pictures on very thin paper containing a very low percentage of ash constituents. The ink used in printing is composed of enamel colours (such as already described), suspended in a medium of very fusible cover mass in just sufficient quantity to fix the colours on in the operation of firing. In this way highly artistic pictures are attainable by the usual methods of printing, and are transferred to the surface of the white-enamelled ware by slightly damping the paper on the back of the printed sheet, laying this smoothly on the ware and when dry, firing it at a heat just sufficient to fix the colours.

A good instance of the possibility of making an immense number of articles of one pattern and style of decoration by this method is afforded by the mugs made for the coronation of the Czar Nicholas II., and for the Jubilee of the Austrian Emperor, Franz Joseph I.

IMITATION CLOISONNÉ TRANSFERS

Another form of decoration produced by the aid of the printing press is that of transfers simulating the well-known cloisonné enamel, and highly suitable for the embellishment of decorative cast iron for building purposes. The pictures are printed in various colours, and the border lines, which in real cloisonné work exhibit a metallic lustre, are black; the printing is managed in such a way that the colours are laid on as thickly as possible.

When a sheet of this transfer paper is applied to an iron surface (which may be moulded, in the form of a rosette, cornice moulding, etc.), and the back of the paper is damped, the latter can be drawn off in a short time, leaving the coloured enamels adhering to the metal. By firing they become so firmly fixed that the colours retain their freshness even after exposure to the weather for years.

XXV.

SPECIALITIES IN ENAMELLING.

Sundry methods of enamelling have been brought forward which differ from, and, according to their inventors, give better results than the ordinary processes described in the foregoing pages. Out of the large number of recipes available in this connection the following have been selected by the author as being of approved practical value, many of the others tried by him having yielded nothing but unfavourable results even when performed with minute attention to details.

IRON GLAZE.

This process was originated by Paris, and is useful as a cheap covering for protecting iron pipes from the destructive influences to which they are exposed when embedded in the ground. The composition of the glaze is as follows:—

Powdered crystal glass	130 parts.
Soda	20·5 ,,
Boric acid.	12 ,,

The materials being carefully mixed together, fused in crucibles, quenched, and reduced to a very soft powder by stamping and grinding.

The iron pipes or other articles to be coated are cleansed by pickling in the usual manner, dried, and coated with a thin layer of gum arabic, or other agglutinant, the powdered glaze being then dusted over them by means of a sieve.

The next stage is to dry the articles thoroughly in a chamber heated to about 150° C., and then bring them to dark red heat, at which temperature the glaze fuses. When properly applied the glaze sticks very firmly to the metal and effectually resists all external influences. Though excellent for iron pipes, for which such a power of resistance is desired, this process—termed by its inventor "*Emaille de fer contre-oxydé*"—is too expensive for general use.

EMAILLE PLAQUÉ-VITRO-MÉTALLIQUE.

Paris also rendered his method available to some extent for artistic purposes by describing a process for durably coating iron with other metals. With this object the iron surface, covered with glaze as above, is brushed over afresh with gum, over which very thin sheets of metal foil (gold leaf, silver foil, copper foil, platinum foil) are laid and fired.

Although in itself good, the metallic coating being extremely durable, the process is hardly likely to be of practical use now that metal can be covered with and preserved from rusting by nickel-plating.

ENAMELS FOR SHEET-IRON LOAF-SUGAR MOULDS.

A very useful enamel mass for sugar moulds, or indeed any sheet-iron ware, is composed of—

Green bottle glass	49 parts.
Fused borax	4 ,,
Litharge	47 ,,

ENAMELLING TUBES FOR STEAM BOILERS.

Owing to the property exhibited by enamelled tubes of iron, copper, or brass, of either entirely preventing the deposition of boiler fur or else, by reason of their smooth surface, enabling the incrustation to be removed with ease, the use of such tubes for locomotive boilers is continually extending.

Their preparation is, however, attended with certain technical difficulties, which nevertheless may be overcome by means of the process now about to be described. After pickling in fairly strong acid, the tubes are scrubbed clean with cylindrical brushes, and similar brushes are employed to apply the coating of enamel. Firing is effected in muffles of suitable length, but not wider than is necessary for the accommodation of several tubes, laid side by side on supports hollowed out for their reception, so as to facilitate handling by means of suitable tongs.

The ground enamel is fired at a high temperature and the attendant must exercise care, by turning the tubes, to ensure uniform heating throughout. This turning must be performed more frequently during the firing of the cover enamel, to prevent the latter from running and forming a coating of irregular thickness.

Enamelled iron pipes are also excellent for conveying the acid water of mines, as they remain unaltered for years, whereas ordinary iron pipes are corroded in a very short time. Of course the enamel employed for such tubes must be of such constitution that it can effectually withstand chemical influences. Amtmann of Gleiwitz uses the following formula for enamel for this purpose :—

Ground Enamel

Quartz	34 parts.
Borax	15 ,,
Soda	2 ,,

Cover Enamel.

Felspar	34 parts.
Quartz	19 ,,
Borax	24 ,,
Tin oxide	16 ,,
Fluor spar	4 ,,
Soda	9 ,,
Saltpetre	3 ,,

The firing of this cover enamel takes twenty minutes at white heat, and the finished tubes are coated with tar whilst still hot.

PLEISCHEL'S ENAMELS.

Pleischel of Vienna has for many years manufactured enamelled ware coated with leadless enamel only, the composition of the masses—which are also suitable for use on sheet-iron articles—being as follows :—

Silica	30 to 50 parts.
Flint	10 to 20 ,,
Kaolin	10 to 20 ,,
Pipeclay	8 to 16 ,,
Chalk	6 to 10 ,,
Ground porcelain	5 to 15 ,,
Boric acid	20 to 40 ,,
Saltpetre	6 to 10 ,,
Gypsum	2 to 5 ,,

Another of the same maker's formulæ is :—

Quartz	30 to 50 parts.
Granite	20 to 30 ,,
Borax	10 to 20 ,,
Glass	6 to 10 ,,
Magnesia	10 to 15 ,,
Felspar	5 to 20 ,,
Enamel soda	10 to 20 ,,
Lime	5 to 15 ,,
Barytes	2 to 3 ,,
Fluor spar	3 to 10 ,,

These ingredients are prepared in very much the same manner as that already described in these pages, by grinding, mixing, fusing and re-grinding, and the glaze is laid on as thinly as possible. The proportions of the mixture depend on the character of the raw materials and must be determined by experiment, since a granite that contains a large proportion of quartz will require more soda than one that is richer in felspar.

BÖTTCHER'S COPPER ENAMEL.

The enamel mass employed by Bottcher for copper consists of—

White felspar	12 parts.
Unburned gypsum	12 ,,
Borax	1 part

The usual method of firing is adopted, and the enamel adheres very tenaciously to the surface of the copper.

XXVI.

DIAL-PLATE ENAMELLING.

The manufacture of dial-plates for clocks is a special business, and generally consists in covering sheet copper with white enamel. The thin sheet copper, cut to the desired size, is made bright and coated on both sides with perfectly white enamel, in fine powder mixed with water and laid on with a brush. As the enamel used is always very rich in tin oxide it covers well enough to be used in exceedingly thin layers.

Any white enamel of good covering power will do for the purpose, the following being typical mixtures —

Sand	100	100	100
Lead oxide	50	108	167
Tin oxide	50	38	33
Potash	200	20	80

When the mass has been applied, the discs, laid side by side, are thoroughly dried, and a large number are placed on thin slabs of fire-brick and inserted in a glowing muffle where they are left until the enamel is fused. Hereupon they are transferred, slabs and all, to a cooling oven. In this manner a very large number of dials can be finished in the course of a day.

The plates are then subjected to a searching examination, and only such as are perfect and exhibit a perfectly uniform, lustrous surface are looked upon as finished. Frequently some of them are slightly blistered or stained in places, and these must be rectified before they are sent out. The simplest way to remove the small blisters or bubbles is by scouring the plate with fine sand, and reheating in the muffle until the enamel has so far fused again that it forms a coherent lustrous covering when cold. Stained patches must be ground off by holding the dial against a rapidly-revolving disc moistened with water containing very fine sand in suspension. When the stain is entirely removed the place is re-enamelled. It should be stated that such patches will only be met with in any abundance when insufficient care has been taken in selecting pure materials for the enamel mass.

The inscriptions (figures) on dial-plates are of black enamel, which is ground up with lavender oil, painted on and fired. As a rule this coloured enamel has a much lower fusing point than the white enamel, so that it may melt while the latter is still in a solid state, since otherwise it would be impossible to obtain a sharp-edged, clear inscription, as the two enamels would run together in fusing and render the edges washy and ill-defined.

The small dial-plates for watches are usually enamelled on one side only, and must be cooled down slowly after firing, in order that the enamel may retain a certain elasticity and not easily craze or crack. Besides, the enamel for this purpose must have such a low fusing point that there is no danger of the copper being corroded by the fused mass.

To ascertain whether or no this is the case, a finished plate is cut in two, and the edges after being rubbed smooth are examined under a magnifying glass. In the case of enamels of suitable fusing point a sharp line of demarcation is visible between the enamel and the metal, but if too refractory an intermediate layer of a bluish tinge will be noticeable; and, owing to the thinness of the coating, will spoil the colour.

Many dial-plate manufacturers, however, endeavour to produce this intermediate layer, under the erroneous impression that it causes the enamel and copper to adhere more firmly together, which is not the case, besides, they unite so closely under ordinary conditions that no special precautions in this direction are required. (See also Appendix p. 183.)

XXVII.

ENAMELS FOR ARTISTIC PURPOSES.

Enamels play an important part in the arts and artistic industries, and, by reason of the beauty of their colours and their durability, are especially adapted for the embellishment of jewellery and articles of adornment.

In earlier times this branch of art was more studied than at present, and there are still in existence, the product of past centuries, works in enamel that constitute artistic relics of high value. Nevertheless, owing to the present state of chemical knowledge, we are nowadays in a position to produce enamels far superior in point of beauty, purity of colour, and durability, to those of our predecessors

As is well known, strenuous endeavours are now being made to elevate industrial art to a high standard, and great attention is being devoted to works in enamel.

Gold and silversmiths, and workers in bronze and metal are again largely resorting to enamels for decorating their productions, and the same applies, to a not inferior extent, to the use of enamel in the manufacture of artistically embellished pottery.

So far as the composition and employment of enamel masses for artistic purposes are concerned, there is little deviation from the methods already described as practised in the industrial world, the principal difference being that the very purest materials obtainable are sought after, since it is from these alone that enamels of handsome colour can be prepared. The more expensive first cost of such enamels is a very minor consideration, the quantity used being in any case very small.

As enamels for artistic purposes are not required to exhibit any special resistance to chemical agencies, they are usually compounded of fusible materials, it being easier under these conditions to employ certain pigments and retain their beauty of colour under the firing process.

The composition of enamels being nowadays a matter of general knowledge, it is easy for makers whose enamels enjoy a particularly good reputation—as is the case, for instance, with the Venetians—to maintain their products at a standard of perfect beauty if they only bear in mind the factors just referred to.

The lowest possible limits of fusibility can be imparted to enamels by the use of glass masses rich in lead, and these are quite unobjectionable in the case now under consideration, since the low resistance of the products is not a source of danger. The subjoined recipes for artistic enamels have stood the test of practice, and it may be stated in this place that these enamels may be used in various ways, the mass being either applied and fired in a single operation, or else a white ground mass is first put on and afterwards covered with the coloured mass. When the enamel is all of one colour the former method may be pursued, but when it is a question of enamel paintings the object is first coated with white mass, which serves as a ground for the subsequent painted decoration.

WHITE ENAMELS FOR JEWELLERY.

Two parts of tin and one of lead are calcined together and entirely converted into the respective oxides; 1 part of the mixed oxides is then mixed with 2 parts of pulverised white crystal glass and fused in a crucible along with a minute quantity of saltpetre or manganese dioxide as a decolorant, the molten mass being afterwards poured out into cold water. This fusing and quenching are repeated two, three, or even four times, until the mass is free from bubbles and quite homogeneous. After being ground to fine powder it may either be applied direct to the object, or, when intended for covering very small surfaces, is ground in lavender oil and laid on with a brush in the same manner as artist's colours.

A white enamel of still lower fusing point may be prepared by the following recipe:—

Tin-lead oxide	100 parts.
Pure quartz meal	60 ,,
Common salt	25 ,,

The pure quartz meal may be replaced by sand, but the latter will have to be specially purified if it is to yield a perfectly white product. With this object 100 parts of sand are fused with 25 parts of common salt, some of the chlorine in which unites with the iron in the sand to form a product, which is volatilised by the heat employed and leaves behind a fritted mass sufficiently free from iron. After this the sand is fused with 25 parts of pure minium, whereby a frit of lead-soda glass is obtained.

To prepare an enamel by the aid of this mass it is reduced to very fine powder and mixed with pure tin oxide (or tin-lead oxide) in the proportion of 50 parts of frit to 100 of oxide; the larger the proportion of the latter the thinner the layer of enamel of good covering power obtainable.

Enamel masses free from tin oxide can also be prepared, in which case sodium antimonate is generally used. The latter, however, in presence of glasses containing lead, yields enamels of inferior appearance; consequently the mass should be prepared by fusing the sodium antimonate with crystal glass only. A very fine enamel is obtained by mixing 3 parts of glass and 1 part of sodium antimonate, with a small quantity of saltpetre.

In the preparation of all these enamels care should be taken, when fusing the materials, to prevent the access of reducing gases to the contents of the crucible, by covering the latter with a close-fitting lid, otherwise an inferior enamel will be sure to result.

RECIPES FOR COLOURED ENAMELS.

A good ground for backing coloured enamels is furnished by—

Sand	3 parts.
Chalk	1 part.
Calcined borax	3 parts.

This mass is particularly suitable for use under pale red, purple red, and blue, as well as other delicate colours, since it exerts no injurious influence on the pigmentary substances.

A somewhat refractory mass, also useful for the same purpose, is obtained from—

Quartz meal	60 parts.
Alum	30 „
Common salt	35 „
Minium	100 „
Magnesia	5 „

TRANSLUCENT COLOURED ENAMELS.

For artistic purposes (painting in enamel) use is made of certain colours, which, for the production of particular shades, have to be translucent. A few recipes for these, as given by Deck, the technical director of the Sèvres porcelain works, are appended below.

Flux or Ground Mass.

	Soft.	Hard.
Quartz	4·5	5·0
Potash	1·5	1·5
Soda	7·0	7·0
Minium	3·5	3·0

Yellow Shades.

	Ochre Yellow	Ivory Yellow.	Opaque Yellow.
Soft ground mass .	9	26	9
Quartz .	4	10	4
Minium .	2	13	5
Ferric oxide (yellow) .	2	1·5	0·8
Antimony oxide .	-	—	0·8

Greens.

	I	II.
Sand	3·5	3·0
Minium	5·5	5·5
Borax	0·5	0·5
Potash	0·5	1·0
Cupric oxide	0·4	0·4

	Gmelin Green	Olive Green
Soft flux	9	90·0
Cupric oxide	1	3·4
Ferric oxide (yellow)	1	6·0
Sand .	4	—
Minium	5	—
Manganese dioxide	-	2·5

Blues

	Lapis lazuli	Turquoise
Flux	50·0	93·0
Cobaltic oxide	0·5	—
Cupric oxide	2·5	7·0

	Garnet	Violet
Flux	11·0	50·0
Antimony oxide	1·0	—
Manganese dioxide	3·0	0·5
Saltpetre	2·5	—
Soda	2·5	—
Cobaltic oxide .	—	3·5

For painting on enamel it is advisable to keep a stock of the various colours prepared in the form of strongly coloured glasses. With this object in view a fusible enamel mass, free from covering ingredients (tin oxide or lead oxide), is compounded, and with this the pigmentary oxides are incorporated. After fusing, the mass is pounded to coarse powder and remelted, the cycle of operations being repeated until a glass of perfectly uniform colour throughout is obtained. This is finely powdered, and for use is ground in lavender oil and applied by the brush to a surface of pure white refractory enamel. On the completion of the painting, the article is carefully fired in the muffle at a heat just sufficient to melt the coloured enamels, which object being effected the temperature is at once reduced in order to prevent the colours running one into another

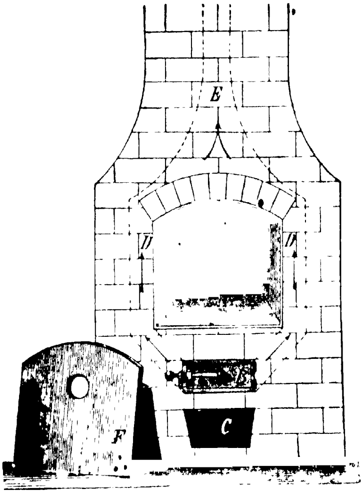

FIG. 16

If any part of the painting does not come up to expectation, it may be removed by careful scraping with a very hard graver, and painted anew it is, however, difficult to perform this operation without damaging the appearance of the painting.

The fusible coloured enamels may be fired in the muffle shown in Fig 13 or that represented in Fig 16. This muffle is placed in a blast furnace having a strong draught and heated by coke or charcoal The gases from the hearth, *B*, surround the muffle in the flue, *D*, and then escape to the chimney, *E*. While the pieces are being fired, the muffle is closed by a fireclay plate, *F*, which is fitted with a peep-hole.

CLOISONNÉ ENAMEL.

This method of enamelling is peculiar, and furnishes products of illimitable durability. As a rule it is practised on copper or gold, and the procedure adopted by the artists of old, and but recently discovered anew, is followed. The outlines of the design to be carried out in enamel are marked on the metal plate in such a manner that a very thin band of metal remains between the edges of every two adjacent coloured enamels, the space enclosed by the outlines being hollowed out by the graver so as to leave a rough surface for the enamel to adhere to. In the case of gold articles, the outlines are also cut out of thin sheets of metal and welded on to the base plate by heat.

The cells prepared in one or other of these ways are then filled with a thick paste of enamel mass and lavender oil (or water) which is fired in the muffle, and the operation is repeated until the cells are completely full of the fused enamel, whereupon the surface is ground and polished.

Similar results can be produced in a more direct way by pressing the fused enamel into sharp-edged metal moulds, setting the pieces in metal in a suitable manner, and finally heating the finished article until the enamel begins to fuse, grinding and polishing the surface when cold again.

The so-called "*émaille champ-levée*" is prepared by stamping a design with steel dies on sheet gold and filling the recesses with enamel, which is then fired. However, of all these methods, cloisonné is undoubtedly the best, on account of the durability of the product.

RECIPES FOR ENAMELS OF VARIOUS COLOURS.

Certain colours will not show up in their full beauty unless applied on ground layers of particular composition. Red from gold purple is peculiarly sensitive in this respect, as is also the yellow produced by antimony preparations; whereas cobaltous oxide and chromic oxide can be easily brought into such a condition that they are applicable to any enamel. This result is obtained by heating the said oxides to a very high temperature, whereby they become almost entirely insoluble, prolonged boiling in strong acids being necessary to effect their solution.

This property of the two oxides in question can be utilised advantageously for producing durable colours on enamels subject to considerable wear. In such event the ground mass is painted over with chromic oxide or cobaltous oxide—strongly calcined ferric oxide behaves in a similar manner—and a thin layer of transparent glaze or cover enamel is fired over it. The colours are then protected—like the strong-fire underglaze colours in porcelain painting—by the cover enamel, and cannot be corroded until the latter is entirely worn away. Of course the ground mass must be rendered opaque, so that the underlying metal does not show through.

In colouring enamel with gold purple, care must be taken to use none but masses free from lead or tin, otherwise no purple will be produced. The frit for this purpose should be prepared from flint meal, chalk, and borax, and is therefore a glass coloured by means of gold purple. The most suitable proportions for the frit are: silica 3, calcined borax 2, chalk 1 part, and, to obtain satisfactory results, a minimum firing temperature must be employed, the gold being reduced and furnishing only a discoloured brown if the heat be too great.

The frit generally used for yellow is prepared direct from: antimony oxide 1 part, alum 1, sal ammoniac (ammonium chloride) 1, and lead oxide 1 to 3 parts. These ingredients are finely powdered, intimately mixed by grinding in small quantities in a mortar, and then slowly heated; the sal ammoniac is gradually volatilised in the form of dense white fumes, and when these have all disappeared the mass is ready for use and will furnish a yellow colour. It is fired with a flux of silica, borax and lead oxide, in quantity equal to, or at most not exceeding double its own weight. All pigments containing antimony or lead oxide require only a small quantity of frit.

The most handsome violet is obtained from manganese dioxide, provided care be taken that no organic matter is present in the mass when fired, and that no reducing gases obtain access; otherwise the dioxide will be easily reduced and give only a brownish colour in place of violet.

When, as frequently happens in enamelling jewellery, small quantities of enamel have to be melted before the blowpipe, the various properties of the enamel masses and the contained pigments must be sufficiently borne in mind. As already described, the inner blowpipe flame has a powerful reducing action, only the outer flame being an oxidising one; consequently the latter alone must be used in enamelling, except in a few rare instances, such, for example, as when a green (ferrous oxide) enamel or a cuprous oxide red mass is to be fired. In such cases the oxidising flame would convert the ferrous or cuprous oxide into the ferric or cupric state, and would change the green of the former to brown red and the red of the cuprous oxide to green.

APPENDIX.

DIAL ENAMELLING

THE art of covering plates of metal with enamel is of great antiquity; it was practised by the Egyptians, and by them probably transmitted to the Greeks and Romans. Several ancient specimens of curious workmanship prove its existence in Britain at a very early period. It was formerly employed chiefly for ornamental purposes, but since the invention of clocks and watches its usefulness has been proportionately increased. For clocks and dials there is probably no substance that could be substituted that can equal enamel in permanence and beauty The art of dial-plate enamelling is divided into two branches, namely *hard enamelling* and *soft* or *glass enamelling*. In the first branch the *Venetian* enamels are chiefly employed; in the last the *English* or *glass* enamels. The practice of *hard* enamelling requires more skill, time and labour than the others, and is consequently the most esteemed. The metals to be enamelled on are usually gold, silver, or copper, but, the process being similar, one description will suffice. The copper, which is the metal usually employed, being evenly flattened in long slips and to a proper thickness, pieces are cut off for use according to the size wanted, they are then annealed in a clear fire in order to make them sufficiently pliable to take the required forms which are given to them by means of brass dies. A complete set of dies varies in size from about three-fourths of an an inch to two inches and a half, the gradations being very small. The copper is next placed on the die best adapted for the purpose and the eye or centre hole is made with a small round-headed punch and smoothed with a grained file, it is then again placed on the die and pressed gradually open till it nearly fills the hole with an oval burnisher; it is afterwards pressed tighter into the hole with a round broach the burr being occasionally taken off by the file, and care employed to prevent the eye from cracking. The punch, burnisher, and round pin are all of steel, the two latter taper in regular gradation towards the handles. When the eye is completed, the edge of the copper is cut round so as to leave a small part projecting beyond the die, which is then turned up or burnished against the edge of the die, the copper being first laid smooth and flat by the burnisher. The copper is then gradually set up to the convexity or height required by rubbing it gently yet firmly with a bent or setting spatula formed of a thin slip of steel about five inches long properly fixed, after which the feet are soldered on. The inconveniences that attended the use of plain copper wire soldered with spelter (zinc) for the feet are now entirely obviated by employing copper wire plated with silver. The feet must be cut by fixing an iron peg into the work board, and the pieces of plated wire being held against it, it will be found to form a very good resistance against the action of the file. It should be observed that, if coppers are to be made for flat plates, the feet should be filed at right angles, but if the plates are convex they should be filed at an angle as nearly as possible corresponding with the curve formed in the hollow part of the copper, because, when the foot is placed on the copper, it will be found to stand perpendicular to the base line or edge of the copper. In order to make the feet remain in their places and facilitate the soldering, the end of each foot before putting it on the copper, which is done by means of a pair of corn tongs or tweezers, is dipped into a slight wash of borax and water through which it adheres with sufficient force to admit of its being exposed to the power of the blowpipe. The lamp in common use contains from a pint to a quart of oil, and has a cylindrical spout projecting about three inches, being an inch or more in diameter. This space is filled with cotton which, being lighted, a strong flame is produced. The copper is carefully placed upon a piece of solid charcoal long enough to be held in the hand, and the flame being then propelled by the blowpipe against the solder or silvered wire as the case may be, the feet are firmly united to the copper. The whole is then thrown into the pickling pan in order to free it from the scale or oxidisable covering acquired from the heat The coppers being thus prepared, the next process is that of enamelling properly so called. The operations of hard enamelling and glass enamelling are, to a certain extent, the same. Where they are different we shall describe the difference as we proceed. The enamel, as it comes from the makers, is generally in small cakes from four to five or six inches in diameter. It is first broken with a hammer and then ground in a mortar and moistened with water, after which the coppers, having been first cleansed by the pickle and carefully brushed out with water, are spread face downwards over a soft cloth or smooth napkin, and a thin layer of hard enamel, called in its ground state the backing, is spread over the under sides with the end of a quill properly cut or with a small bone spoon. The coppers are then slightly pressed on by another soft cloth or napkin, which, by imbibing some portion of the water, renders the enamel sufficiently dry to be smoothly and evenly spread with the rounded side of a steel spatula The next operation is to spread a layer of glass enamel over the upper sides of the coppers called the *first coats*. In doing this the surface is first brushed slightly over with a small camel-hair brush or a hare's foot to remove any dirt or extraneous particles of enamel, as the mixture of any hard enamel with the glass would infallibly spoil the work. The glass is then spread upon the coppers in a layer, the thickness of which is commonly the same as the height of the edge and eye. The water is afterwards slightly absorbed with a clean napkin smoothly folded, and the enamel spread by a thin *flat spatula* till all unevenness is removed and the surface lies regularly from edge to centre. The next department is *firing*, as it is technically called, which consists in melting it till it becomes one uniform mass on the surface of the copper. In doing this, the first coats are placed upon rings which are generally made of a mixture of pipemakers' clay and Stourbridge clay rolled up into the form of cylinders and turned in a lathe by means of a cylindrical piece of wood forced through the centre of the mass when wet. They are next put into a shallow tin vessel called a tin cover which is either made square or round according to the fancy of the artificer, and is commonly about three-quarters of an inch in depth. All the moisture is then slowly evaporated from the enamel by placing the cover upon a German stove or in some other convenient situation near a fire where the evaporation can be properly regulated. The firing is executed beneath a muffle placed in a small furnace ignited with coke and charcoal. The furnace being drawn up to a sufficient heat by means of a register, the *first coats* are taken separately from the tin covers and placed upon thin planches of clay or iron chalked over, and gradually introduced beneath the muffle, where, in a very short time, the enamel melts or *runs*, and, becoming properly consolidated, the first coat is complete. A second layer of ground enamel is then gently spread with a quill and prepared for firing by the napkin and spatula as before, after which the second coats are placed upon the rings, and the moisture being evaporated in the tin cover, they are ready for a second fire. This requires an equally cautious management as the former one. The plates must not be overfired nor must the heat be suffered to melt the enamel too rapidly, but a kind of rotary motion called coddling must be given to the work by holding the loaded planch lightly with the tongs, and gently drawing the edge of it towards the mouth of the muffle, and then returning it to its former place till the fusion be complete. The work is now in a fit state for polishing, technically called using off. This is performed by rubbing the surface of the plate on a grit stone with fine sand and water until all the glazed appearance is completely obliterated, and one uniform and equally rough surface is produced. The intention of this part of the process is to remove the mottled appearance on the surface and give a more equal convexity to the plate.

HARD ENAMELLING.

The foregoing is an outline of the process for glass enamel plates. The firing of the Venetian hard enamel is much the same, but the heat applied to melt it must not be so great, and the plate must be taken from the fire as soon as the enamel is found to form one tolerably compact body, as any longer continuance would have a tendency to spoil the intended shape of the plate which is always considered a most essential quality in those of hard enamel. The heat for finishing may be rather more than that used in the first fires, as in that instance the intention was only to unite the particles of the enamel into one solid mass; but the principal object in finishing being to raise the flux to the surface as much as possible, a greater heat may be used with advantage, but the plate must be taken from the furnace the instant that the surface appears bright and glossy. Where good Venetian enamel cannot be obtained and mixtures of various kinds are resorted to, it frequently happens that the glass enamel plates crack when they are brought to the second fire. When this is the case, as soon as the crack is observed, the plate must be withdrawn from the fire, and if it extends only from the centre hole to the edge it will in most cases bear mending, but if it has happened in two or three places it will be useless to make the attempt, as it will rarely succeed If the dial-plate was to continue in the fire after it is cracked a sufficient time, the enamel would close and the plate become sound again, but as the copper on its surface is in a state of oxidation, the oxide of copper uniting with the enamel would rise to the upper surface of the plate, producing by its union a faint and sometimes a dark-green line which would evidently render the plate useless. The operator therefore must observe the time when the crack has opened to its greatest width, and before it unite or close at the bottom the plate must be withdrawn from the furnace and allowed to cool. The opening must then be filled with fine enamel laid sufficiently high to allow for its running down in the fire, but to adjust the quantity so as to prevent the appearance of a seam across the plate, will require much judgment and, indeed, however well the operation may succeed, it will still remain visible.

The method of painting in enamel is performed on plates of gold, silver, and copper, enamelled with the white enamel whereon they paint with colours which are melted in the fire, by which they acquire a brightness and lustre like that of glass. This painting is the most prized of all for its peculiar brightness and vivacity which is very permanent, the force of its colours not being effaced or sullied with time as in other painting, and continuing always as fresh as when it came out of the workman's hands.

THE END

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